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IRON AND STEEL

OUTLINES OF INDUSTRIAL
CHEMISTRY.

A SERIES OF TEXT-BOOKS INTRO-
DUCTORY TO THE CHEMISTRY
OF THE NATIONAL
INDUSTRIES.

EDITED BY
GUY D. BENGOUGH, M.A., D.Sc.

OUTLINES OF INDUSTRIAL CHEMISTRY.

IRON AND STEEL

AN INTRODUCTORY TEXT-BOOK FOR
ENGINEERS AND METALLURGISTS

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WITH A SECTION ON CORROSION

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PREFACE

IN this small book an attempt is made to present in as short a manner as possible the more important principles of the metallurgy of iron and steel, and it is hoped that engineers and other users of these metals, as well as students of metallurgy, will find something of value in its pages. Practical details of the methods of production have been avoided almost entirely, in order that more attention may be devoted to such matters as an explanation of the constitution of steel and cast iron and the effect of mechanical and heat treatment on the properties of these alloys. The important subject of corrosion of steel and iron has been fully dealt with in a section specially contributed by Dr. Bengough, the editor of this series.

The author wishes to tender his thanks to Mr. L. A. Gross, B.Sc., and Mr. J. L. Haughton, M.Sc., for some of the drawings and diagrams and for help in the preparation of the subject-matter, for which purpose the standard text-books, particularly Professor Turner's "Metallurgy of Iron" and Mr. F. W. Harbord's "Metallurgy of Steel," have been freely used as sources of information. Grateful acknowledgment is also made to The Daimler Company of Coventry, through Mr. T. W. Picken, for their kindness in supplying drawings of furnaces used in case-hardening and for the diagram and photograph of the malleable oven built by Messrs. Gibbons Bros., whose permission to make use of the diagram was readily given; to the Iron and Steel Institute for permission to reproduce the diagram of the blast furnace, and to Professor S. M. Dixon, M.A., M.Sc., for the diagram of the testing machine.

O. F. HUDSON.

THE UNIVERSITY, BIRMINGHAM,
November, 1912.

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IRON AND STEEL

AN INTRODUCTORY TEXT-BOOK FOR
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SECTION I

CHAPTER I

INTRODUCTORY—MECHANICAL TESTING

THE purest iron that can be obtained is a comparatively soft, very ductile and malleable metal having pronounced and characteristic magnetic properties. In this condition iron has only a limited range of usefulness, but its properties may be so profoundly altered by small, sometimes minute quantities of other elements that its alloys are by far the most important of the metallic materials with which the engineer has to deal.

Broadly speaking, iron and its alloys may be classified as cast iron, wrought iron and steel. Cast iron is not malleable or ductile, and, as its name implies, is used only in the form of castings; for which purpose its comparatively low melting point (commonly about 1100°C. to 1200°C.), and the fluidity of suitable brands when melted, eminently fit it. It has also other characteristically useful properties, such as rigidity, power to resist compression and ability to give good wearing surfaces. As a rule it contains at least 2.5 per cent. of carbon and usually considerable quantities of other impurities.

Wrought iron, which usually is almost free from carbon, and is malleable, ductile and tough, forges well and repeatedly, and its welding qualities are unsurpassed. Although to a large extent now replaced by mild steel, it is for a number of purposes the best and most reliable material that can be used.

Steel is the name given to a series of iron alloys of widely varying character, and may itself be conveniently classified as mild steel, medium steel, tool steel and special steels. Mild steel, which is made and used in enormous quantities for structural work, is very malleable and ductile, and readily welded, but it cannot be greatly hardened by quenching. It contains only small quantities of carbon—up to about 0·3 per cent.—and in this respect does not differ greatly from wrought iron. Its method of manufacture, however, is quite unlike that of wrought iron, particularly in the fact that it is produced in the fluid condition and cast into ingot form before being rolled or forged. Medium steel contains more carbon—up to about 0·75 per cent.—and is stronger and less ductile than mild steel. It is capable of being hardened by sudden cooling from a red heat, although most medium steels, such as rails, axles, tyres, etc., are used in the unhardened state. Tool steels (or high-carbon steels) contain from 0·75 per cent. to 1·5 per cent. of carbon, and are mainly used in the hardened and tempered condition. Although ordinary steels may thus be classified according to the amount of carbon they contain, there are no sharp lines of division, the whole forming an unbroken series of alloys. The fourth class of steels—the special steels—are iron alloys with varying amounts of carbon and containing considerable, often large, quantities of other metals such as manganese, nickel, chromium, or tungsten.

Testing.—The suitability of any kind of iron or steel for a particular purpose is judged very largely by its behaviour under various mechanical tests. The consideration therefore of some of the principles of mechanical testing and the deductions to be made from the results is of the greatest importance, both to the metallurgist and the engineer. It is the aim of the metallurgist to fulfil the most exacting requirements of the engineer by a careful and intelligent control of the processes of manufacture, and it is the duty of the engineer so to frame his specification as to ensure the supply of a safe and suitable material. It is thus to the interest of the manufacturer to study carefully the needs of the engineer, who in his turn should possess some

knowledge of metallurgical operations and of the chemical physical and mechanical properties of the metals he uses.

The mechanical tests applied to iron and steel may be classified generally as "Cold Tests," and "Hot Tests," the former being used to test the strength, ductility and other properties of the material at the ordinary temperature, and the latter to test its forging qualities and its strength at temperatures more or less raised above the normal.

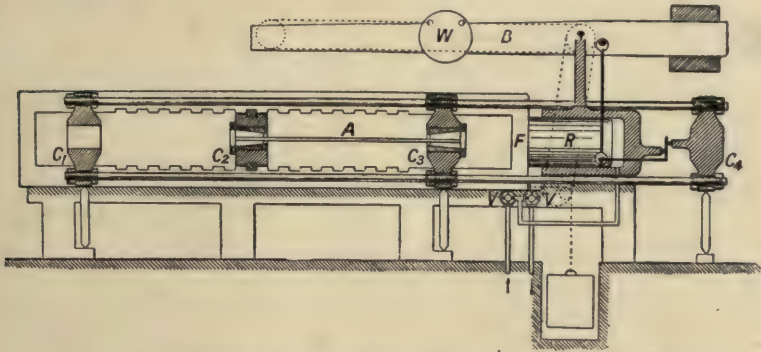


FIG. 1.—Diagram of Horizontal Hydraulic Testing Machine.

A is the tensile test-piece held by suitable grips in the cross-heads *C*₂ and *C*₃. The load is applied by the ram *R* through the frame *F* to the cross-head *C*₂. The cross heads *C*₁, *C*₃ and *C*₄, are screwed to the horizontal bars, and supported are knife edges as shown. In a tensile test the load is taken up by the cross-head *C*₃ and transmitted through the horizontal bars, cross-head *C*₄ and the system of levers (shown by heavy black lines) to the beam *B*, where it is balanced by the movable weight *W*. *V* and *V'* are the valves controlling the supply of water to the cylinder. In making compression or transverse tests the cross-heads *C*₁ and *C*₂ are used.

Tensile Tests.—The most widely used of all the cold tests is the tensile test, in which a gradually increasing stress is applied in the form of a direct pull, and its effect observed up to the point at which the test piece fractures. For very small sections, such as wires, the tensile stress may be applied directly by means of weights, but such a method is inconvenient in any case, and impracticable for large loads. Specially designed machines are therefore used, in which the tensile stress is applied by hydraulic or mechanical power.

A tensile testing machine consists of a hydraulic ram or a screw to which one end of the test piece is fixed, the other end being attached to a lever or system of levers, carrying a comparatively small weight. The load is applied by the screw or ram and is balanced and measured by adjusting the position of the weight on the lever which always remains horizontal as the ram or screw takes up the extension of the bar. Testing machines may be made to test the specimen, in the horizontal

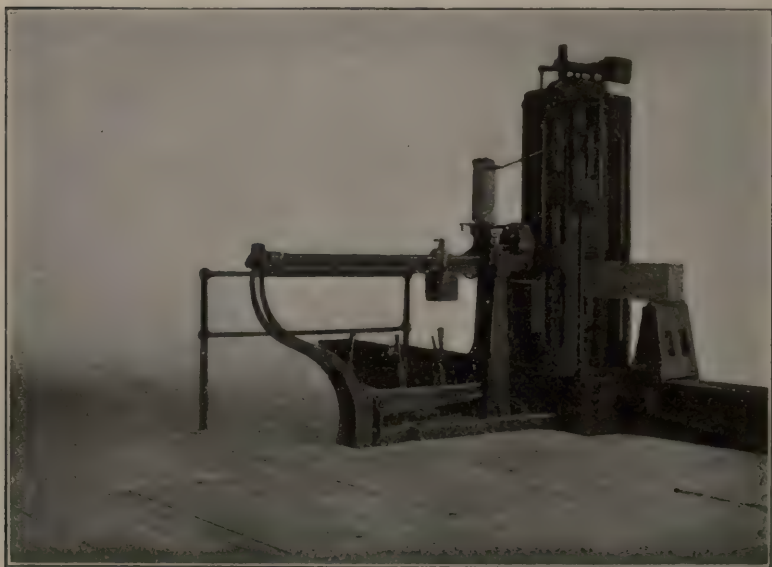


FIG. 2.

or vertical position, and both kinds of machine are in use. Fig. 1 shows diagrammatically a testing machine of the horizontal hydraulic type capable of testing up to a load of 50 tons. This machine, together with a much larger (300 ton) machine of a similar type, is installed in the testing laboratory of the University of Birmingham. Fig. 2 is reproduced from a photograph of a 100-ton vertical testing machine (screw type) in use in the same laboratory. Tensile testing machines may also be used for compression tests and for transverse

tests (*q.v.*), and Fig. 2 shows the machine being used for the transverse test of a beam.

The most desirable form of test piece (Fig. 3) is of circular section and has screwed ends, by which it is held in the grips of the machine. This form, however, is not always possible or convenient, and bars of rectangular section may be used. In any case, the central portion should be accurately turned or machined and joined to the larger section at the ends by curved shoulders. For mild steel and wrought iron, the central parallel portion should not be less than 8 inches, but for cast iron and hard steel the length of this part may be less and is often only 2 inches. If, however, an extensometer is to be used for measuring the extension as the load is applied during the test and thus determining the elastic limit, a parallel length of at least 8 inches is usually necessary. Before the bar is placed in the machine its diameter is carefully



FIG. 3.

measured by means of a screw micrometer at several points in its length, or, if the bar is rectangular, its width and thickness are measured in a similar way. A fine line is then made with a scriber along the whole parallel length, and on this line very light punch marks are made at distances of 1 inch. For ordinary purposes it is generally sufficient to make two marks, the distance between them being that over which the extension is to be measured. After testing the two ends of the test piece are carefully fitted together, and the percentage elongation determined by accurately measuring the distance between the punch marks. The area of the section at the point of fracture is also measured and the percentage contraction of area determined. In reporting the elongation of the specimen it is necessary to state the distance on which it was measured, as the test piece does not stretch uniformly throughout its length, a considerable local extension occurring in ductile materials in the neighbourhood of the fracture.

A complete tensile test should furnish sufficient data for the construction of a stress-strain diagram in which ordinates and abscissæ are tons load and percentage elongation respectively. The curve so obtained shows graphically the behaviour of the metal during the test. Fig. 4 represents an ideal stress-strain diagram for rolled mild steel. From A to B the curve is a straight line, the stress and strain being proportional. During

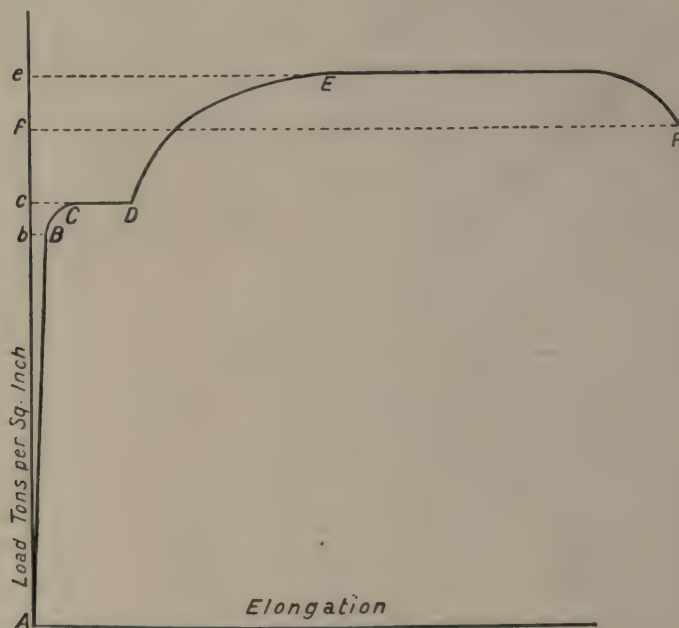


FIG. 4.—Stress-Strain Diagram.

this period the steel is within the elastic limit, and on taking off the load the test piece returns to its original dimensions. At the point B the elastic limit is reached, and any increase of stress causes a permanent distortion. Beyond the elastic limit the elongation increases rapidly with increase of stress, and the curve departs from the straight line form it has hitherto maintained. At C, under a stress a little above the elastic limit, the bar elongates suddenly and to a comparatively very great extent, from C to D, without any increase of stress.

This point, C, is known as the yield point and is easily observed during testing by the sudden drop of the beam. The yield point is very commonly taken as the elastic limit, and in many cases (*e.g.*, mild steel) it is not far removed from the true elastic limit. It must, however, be remembered that this is not so for every material, and may not be even approximately true. Thus, annealed alloys such as 70:30 brass show, if at all, only a very indefinite yield point which may bear little relation to the elastic limit. The elastic limit, therefore, should, if possible, be determined as well as the yield point, especially as it is really the more important figure. After the sudden elongation at the yield point the steel appears to stiffen again, and from D to E an increase of stress is required to produce a further elongation. The maximum stress is reached at E and the test piece again increases rapidly in length without any increase of the load. The test piece now begins to neck or show a marked contraction of area in the neighbourhood of the point at which fracture is about to occur. Owing to this contraction of area about the point of fracture the breaking stress is lower than the maximum stress, as shown by the downward slope of the curve to the point F.

Transverse Tests are not often made on steel, except in special cases such as girders, but for cast iron they are among the commonest mechanical tests. For steel the ordinary transverse as well as shearing tests, which are sometimes made, can be made in the tensile testing machine, but frequently special machines of a simple character are used for the transverse test of cast iron. The cast iron test bar is commonly 3 feet by 2 inches by 1 inch. It is supported at the ends and weighted at the middle until fracture occurs, the amount of deflection being noted.

Compression Tests.—The power of cast iron to resist crushing is of such importance that compression tests of this material are of great value, while steel also is sometimes with advantage tested in compression (the test pieces used being small cylinders or prisms). Since, however, the crushing strength of cast iron is some five or six times as great as the tensile strength (the average crushing strength is given by Turner in his

"Metallurgy of Iron" as 40 tons per square inch), it is not always necessary to make special tests.

Bending Tests.—The quality of wrought iron and steel is also frequently tested by a cold bending test made either by pressure or hammering. The test piece is bent over a round bar, the radius of the bend being specified for most purposes as 1.5 times thickness of test piece, and should show no sign of fracture after bending through a specified angle. For plates the angle is usually 180° and for dead mild steels the bend is also hammered close.

Impact and Alternating Tests.—In the tensile and other tests which have so far been considered the stress is applied gradually, but the conditions under which the material is to be used frequently require that it should be able to resist sudden shock or rapid alternations of stress. Testing on these lines has been considerably developed in recent years, and many impact and alternating stress machines have been devised, although shock tests under a falling weight have always been adopted for rails, tyres and axles, and their value fully recognised.

In modern impact machines the test bar is notched or grooved and is fractured by a falling weight. The shape and position of the notch vary in the different methods; one or a number of blows are given; the test bar is supported at both ends and the blow applied at a notch in the centre of the bar, or the bar is held at one end in a vice and the blow applied at the other end. One of the simplest and best known impact machines is Izod's,* in which a small test piece 2 inches long, $\frac{3}{8}$ inch wide, and $\frac{5}{16}$ inch thick, and having a V-shaped notch $\frac{1}{20}$ inch deep, is held by one end in a clip or vice. The free end of the test piece is struck by a pendulum released from a definite position, and the arc through which the pendulum swings after fracturing the test piece is measured. The energy absorbed in breaking the material is thus determined.

In Stanton's † machine a number of blows is given to a test bar $\frac{1}{2}$ inch thick, grooved at the centre and supported on knife

* British Association Reports, 1903.

† Seventh Report of the Alloys Research Committee, Proc. Inst. Mech. Engineers, 1905, p. 897.

edges $4\frac{1}{2}$ inches apart. The test bar is struck about 100 times per minute by a hammer weighing $4\frac{1}{2}$ lbs. falling a distance varied at will up to $3\frac{1}{2}$ inches, and is turned through 180° between each blow. The total work done in effecting the fracture of the bar is calculated from the number of blows given (recorded by a counter) and the height of fall of the hammer.

It is well known that rapidly alternating stresses which are below the elastic limit may in time cause the fracture of iron or steel or other metals, and as such conditions frequently prevail in practice, an alternating test of this character is of value. The machine designed by Wöhler,* with whose name this test is associated, consists of a wooden frame carrying in bearings an axle which is rapidly rotated by a belt. Test pieces are fixed horizontally in conical recesses in the ends of this axle, and after being fixed the test pieces are turned to run true. Spring balances, by means of which any required stress can be applied, are attached to the free ends of the test pieces, and the number of revolutions necessary to cause fracture is determined by a counter. As the bar rotates each part of it is subjected alternately to stresses in tension and compression, and sooner or later fracture will occur even under stresses distinctly below the elastic limit.

Another alternating test of a different character is that due to Arnold.† In Arnold's testing machine one end of the test piece (a bar $\frac{3}{8}$ inch in diameter) is fixed and the other end passes through a slot in a reciprocating plunger, in this way subjecting the metal to repeated bendings backwards and forwards. The rate of alternations is 650 per minute, and the distance between the striking line of the plunger and the upper surface of the grip holding the test piece is 3 inches. The quantity measured is the number of alternations before fracture, and as this number never reaches 2,000 the test is rapidly carried out.

Hardness Tests.—Hardness is a property of the greatest

* For an account of Wöhler's work, which was first published in 1871, reference may be made to Unwin's "Testing of Materials of Construction," Ch. XVI., p. 366.

† British Association Reports, 1904, v. also *Engineering*, 1908.

importance practically, but one that is very difficult to express satisfactorily in a quantitative fashion. Hardness may be measured by means of the sclerometer devised by Professor Turner of Birmingham. In this instrument a diamond is fixed at one end of a balanced arm, and the diamond point used to make a series of scratches on the polished surface of the metal to be tested. The weight on the diamond in grams necessary to produce a scratch corresponding to a standard scratch on a standard metal surface is then taken as a measure of the hardness. In Brinell's method, which is very largely used, a hardened steel ball is forced into the surface of the metal to be tested. The maximum pressure applied, divided by the spherical area of the concavity (deduced from its diameter), gives as a quotient a number called the "hardness number." The Brinell test may be carried out in any tensile testing machine that can be used for compression tests.

Hot Tests.—These consist of welding tests and tests of the hot working qualities of the metal. The welding tests commonly used consist of: (1) Lap-welding two pieces of wrought iron or steel, punching a $\frac{1}{2}$ -inch hole through the weld, and then, while hot, drifting this hole to 2 inches in diameter. After such treatment the weld should show no sign of parting and there should be no cracks over the drifted portion of the metal; (2) Two pieces of the metal are scarf-welded and then, while hot, the welded bar is bent backwards and forwards at the weld. The weld should stand five or six bends without any injury.

The tests for hot working consist of: (1) Plating out while hot the end of a bar under the hammer and examining the edges of the plated-out portion. Red shortness is indicated by the presence of cracks. (2) Hammering out the end of a bar, splitting the hammered portion longitudinally and bending back the two parts in ram's horn fashion (Ram's Horn Test). Metal free from red shortness should show no sign of cracking after this treatment at various temperatures.

CHAPTER II

SMELTING OF IRON ORES

Iron Ores.—In iron smelting the metal is obtained by the reduction of ferric or the magnetic oxide, and those ores are used which contain or readily yield a sufficient proportion of these oxides reasonably free from such impurities as sulphur and phosphorus. Phosphorus, which is usually found in iron ores in the form of calcium phosphate, is not removed at all, or only to a slight extent, in the blast furnace, but is retained in the iron as phosphide of iron. In consequence iron ores containing more than a very small quantity (0·04 per cent.) of phosphorus yield a pig iron unsuitable for conversion into steel by the acid Bessemer or acid Open Hearth processes, although iron used for foundry purposes commonly contains over 1 per cent. of phosphorus, and for basic steel making sometimes as much as 3 per cent. Sulphur, on the other hand, is always undesirable, even in small quantities, and, although it may be partially removed in the blast furnace, it is seldom profitable to allow more than a few tenths of 1 per cent. of sulphur to be present in the furnace charge. The amounts of sulphur and phosphorus present will thus largely determine the value of iron ores, and there are other substances, such as arsenic, titanite oxide, etc., which, if present in more than small quantities, may render an ore unprofitable to smelt for iron. It follows, therefore, that extensive deposits such as those of iron pyrites are not available as iron ores, their value depending on the use to which they may be put for other purposes, such as sulphuric acid making. The “purple ore,” however, which is the ferric oxide obtained as a by-product in treating pyrites for their sulphur and

copper, finds its way in considerable quantities to the blast furnace or is otherwise made to yield its iron contents.

The chief iron ores are the following :—

Magnetites	containing Fe_3O_4 .
Red hæmatites	„ Fe_2O_3 .
Brown „	„ $Fe_2O_3 \cdot H_2O$.
Spathic iron ore }	„ $FeCO_3$.
Clay ironstones }	

Magnetites.—When pure, magnetic oxide of iron (Fe_3O_4) is the richest iron ore, containing 72·4 per cent. of iron, and is the form in which the iron occurs in some of the most extensive and valuable deposits in the world, *e.g.*, the magnetites of the Lake Superior District of North America, and the very pure ore from some of the noted mines of Norway.

Red Hæmatites.—Ores which contain their iron in the form of ferric oxide are, broadly speaking, of two classes, *viz.*, those in which it occurs as the anhydrous oxide, *e.g.*, red hæmatite, and those in which it occurs as the hydrated oxide, *e.g.*, brown hæmatite. The red hæmatites, which are usually very free from sulphur and phosphorus, require no preliminary treatment before smelting. Iron made by smelting red hæmatites or other pure ores is commonly known as “ hæmatite iron,” and is used principally for making steel by the acid processes. In this country the red hæmatites of Cumberland and Lancashire are well known as producing hæmatite iron of the best quality.

Brown Hæmatites.—These ores constitute one of the most abundant sources of iron in this and other countries. They are usually more or less phosphoric, the iron being used in the foundry or for making basic steel. The amount of water present varies, and there is no very sharp line of division between red and brown hæmatites as regards general appearance. There are many intermediate varieties between the typical hard, dense, red hæmatites of a dark red or almost black colour, and the soft, friable, brown hæmatites (limonite) of a light yellowish brown colour. Brown hæmatites are

often calcined to drive off the water, and the calcined ore then has a red colour.

Spathic Iron Ore.—In this ore, carbonate of iron ($FeCO_3$) occurs in a state of relative purity and forms large and important deposits in Styria, and is also worked in Germany, notably in Westphalia. Spathic iron ore is usually low in sulphur and phosphorus. Manganese, as in the case of Stryian ores, is often high in spathic iron ore.

ANALYSES OF TYPICAL IRON ORES.*

	Cumberland Red Hematite "Best."	Spanish Hematite Red.	Northampton Brown Hematite.	Scotch Blackband.	Cleveland Ironstone.
Fe_2O_3	85.86	72.10	—	—	3.74
FeO	—	—	—	—	34.04
Al_2O_3	—	.20	5.78	4.20	9.32
MnO	—	.80	—	—	.38
CaO	—	.60	1.85	2.90	5.08
MgO	—	.20	—	4.10	3.65
SiO_2	4.96	6.00	8.13	4.90	10.04
S	Trace	.025	—	—	.13
P	.006	.018	.60	.48	.56
Combined water	—	9.00	} 12.00	—	2.89
Moisture	4.60	11.00		—	9.50
CO_2	—	—	—	—	20.09
IRON	60.10	50.47	40.72	58.40	29.09

Clay Ironstone consists of carbonate of iron mixed with more or less clayey matter. It is usually found in beds in the coal measures, and is mined with the coal, although the best known and largest deposit in this country, the Cleveland ironstone, occurs in the lias beds of the Cleveland hills in North Yorkshire. The clay ironstones of the coal measures contain a moderate amount of phosphorus (good Staffordshire clay ironstones contain about 0.25 per cent.) and give a pig iron particularly suitable for the production of good wrought iron or strong castings. The clay ironstones of this country (Staffordshire, West Yorkshire and South Wales) are, however, becoming worked out, and good qualities are less abundant. Sometimes the clay ironstones

* These and numerous other iron ore analyses will be found in the *Journal of the Iron and Steel Institute*, 1908, Vol. III., pp. 343—359.

are found containing considerable quantities of carbonaceous matter, are black in colour, and known as blackband ores. They may usually be calcined without extra fuel, as in the case of North Staffordshire and Lanarkshire ores. The Clevelandshire ironstone, which contains about 33 per cent. of iron, is much more phosphoric, and the iron made from it contains about 1·6 per cent. of phosphorus.

Preliminary Treatment of Iron Ores.—It is in some cases profitable to adopt special means to concentrate the ferruginous material in the crude ore, and to separate it from impurities, as in the case of certain magnetic ores, but usually the ore either undergoes no preliminary treatment before smelting or is merely calcined. Calcination has for its objects the driving off of carbon dioxide, water, coaly matter, sulphur and other volatile substances, and the conversion of ferrous oxide into ferric oxide. Carbonate ores, such as clay ironstones and blackband ores, are always, and brown hæmatites frequently, calcined. Magnetites and red hæmatites seldom need this treatment and are usually smelted without any preliminary treatment. In certain cases, *e.g.*, blackband ores, where sufficient bituminous matter is present in the ores, they are calcined in open heaps, but usually the operation is carried out in specially constructed kilns, using coal, or in some cases gas, as fuel.

Smelting of Iron Ores.—The only practical method of extracting iron from its ores in large quantities is by means of blast furnace smelting. In this process the iron is obtained in liquid form and cast into pigs or taken direct to mixers in which it is kept in the molten condition for use in Siemens furnaces or Bessemer converters. The gangue, or barren portion of the ore, and the ash of the fuel are at the same time also separated as a liquid slag, fluxes being usually added to this end. It is not, however, possible to obtain iron in a state of purity by these means. The metal produced contains some 5 to 10 per cent. of impurities and is known as cast iron or pig iron.

The Blast Furnace.—This is of the type known as shaft furnaces, in which the fuel, ore and fluxes are in contact.

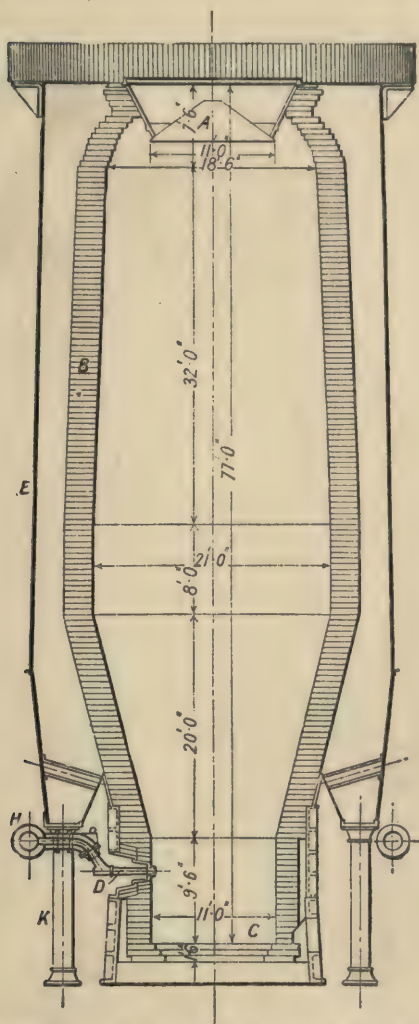


FIG. 5.—Diagram of a modern Cleveland Blast Furnace.*

A Cup and Cone Charging Apparatus.

B Inner Firebrick Lining.

C Hearth.

D Twyer.

E Outer Steel Shell.

H Blast Main.

K Columns supporting Furnace Structure.

The tap-hole, at the lowest level of the hearth, is not shown.

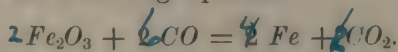
* From "A Description of Messrs. Bell Brothers' Blast Furnaces from 1844—1908," by Greville Jones, *Journ. of I. and S. Inst.*, 1908, Vol. III., p. 59.

The shape and dimensions of a modern blast furnace are shown in Fig. 5. The furnace consists of an outer shell of steel or iron plates E which is lined with fire brick B and supported on a ring which is carried by cast iron columns K. The top of the furnace is usually closed by a cup and cone charging arrangement A. The charge of ore, fluxes and fuel, usually coke, is placed in the cup and admitted to the furnace by lowering the cone or bell. Except for a very short time during charging the furnace is thus kept closed and the gases pass off through the downcomer,* and are burnt partly in the stoves to heat the blast and partly under boilers to raise steam, or, after suitable cleaning, are used in gas engines for power purposes.

The blast enters the furnace through the tuyers D, which are usually six to ten in number, after being heated in the hot blast stoves, except in special cases where "cold blast" iron is being made. The pressure of the blast varies considerably according to the construction of the furnace, character of the charge, etc. In the Cleveland district a pressure of about 5 lbs. per square inch is in many cases found suitable, while in the United States a pressure of 9 or 10 lbs. is commonly used. The temperature of the hot blast is usually between 750° C. and 800° C., but lower temperatures are sometimes used. The molten iron is periodically withdrawn from the hearth of the furnace through the tap hole, and the slag is allowed to run almost continuously through the slag-notch which is at a higher level.

It would be beyond the scope of this book to enter into any lengthy account of the chemical reactions which take place in the blast furnace, but the following very brief outline may be given.

The principal reducing agent in the blast furnace is carbon monoxide (CO) which is present in large quantities in the furnace gases. The reduction of ferric oxide to metallic iron may be summarised by the following equation:—



* The downcomer, which is not shown in the diagram, is connected with an opening in the furnace above the level of the charge (stock line).

A number of reactions are, however, involved, and the first stage of the reduction consists in the conversion of ferric oxide to the magnetic oxide (Fe_3O_4)



The magnetic oxide is then reduced to ferrous oxide (FeO) which in its turn, as the temperature rises, is reduced to metallic iron, the reactions being as follows:—



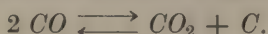
These reactions are reversible ones and the direction in which they proceed will depend on temperature and the composition of the furnace gases. In the blast furnace the course of the reactions is influenced chiefly by temperature, and reduction, which begins well below a red heat and after the charge has descended only a few feet in the furnace, is practically complete at a temperature of $900^\circ C$. In addition to the reactions given above the reduced iron at suitable temperatures is oxidised by carbon monoxide, ferrous oxide being formed and carbon deposited thus:



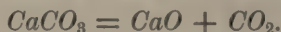
This reaction commences below $400^\circ C$., and is most active just below a dull red heat, thereafter becoming less important and practically ceasing at a red heat. The ferrous oxide so formed is again reduced to metallic iron as the charge descends.

The ferric oxide is thus almost entirely reduced to the metallic state in the upper region of the furnace, and the reduced iron in a spongy condition descends in the furnace in intimate contact with finely divided carbon. Little further action now takes place as the charge descends, except the absorption of carbon by the metallic iron, until the iron melts at about $1,200^\circ C$. and small quantities of remaining ferrous oxide are reduced. As the charge approaches the region of the tuyers and the temperature reaches a white heat the slags form and melt, some silica, all the phosphorus, pentoxide, and most of the manganoú oxide are reduced by solid carbon, and the molten iron becomes further carburised.

Considering now the ascending current of gases, all the oxygen introduced in the hot blast forms carbon monoxide within a very short distance of the twyers, and carbon dioxide produced immediately combining with more carbon to form carbon monoxide. At a distance of only two feet from the twyers no oxygen and no carbon dioxide can be detected in the furnace gases, which contain some 35 or 40 per cent. of carbon monoxide, the remainder being principally nitrogen with a little hydrogen and small quantities of other substances such as cyanides. The cyanides probably play an important part in the reduction of the last portion of ferrous oxide in the lower part of the furnace. As the current of gas ascends and becomes cooler some carbon monoxide gradually dissociates in presence of finely divided metallic iron, thus—



At a red heat also, the limestone added as flux decomposes, giving lime and liberating carbon dioxide, part of which combines with more carbon to form carbon monoxide



The carbon monoxide in the gases reduces iron from the ores as explained, and the waste gases eventually discharged from the furnace contain some 25 per cent. of carbon monoxide.

In the blast furnace there are two zones of reduction of which the more important is that in the upper part of the furnace, where carbon monoxide is the reducing agent, the other being just above the twyers. There are also two sources of heat supply in the blast furnace, the principal being due to the combustion of the carbon of the coke at the twyers, where the temperature is about 1,900° C. The other source of heat is in the upper part of the furnace, and is due to the reduction of ferric oxide, the equation $Fe_2O_3 + 3\ CO = 2\ Fe + 3\ CO_2$ being exothermic.

The materials which enter the blast furnace are partly solid and partly gaseous. The solid charge consists of iron ore, flux and fuel, and enters at the top of the furnace; the gaseous charge or blast of air, usually preheated, enters at the bottom of the furnace through the twyers. The amount of air blown

into a blast furnace varies, but is usually more than equal in weight to the rest of the charge. The ores of iron have already been enumerated; the flux employed is nearly always limestone, and the fuel used is usually coke. In some cases ores or mixtures of ores are smelted in which the gangue or non-ferruginous portion is self fluxing; that is to say, the silica and bases (lime, alumina, magnesia, etc.) in the charge are present in the proper proportion to yield a fluid and otherwise suitable slag. In the majority of cases, however, the addition of limestone is necessary to produce a fluid slag, and one that is rich in lime. Excess of lime is usually necessary in order to remove sulphur in the slag. Besides coke, raw coal of a suitable non-caking character is sometimes used as fuel, and furnaces using charcoal are still worked profitably to produce iron of exceptional quality and purity.

The products issuing from the blast furnace are entirely fluid and consist of liquid metal and slag and waste gases. The metal, of which the composition varies, consists of about 90 to 96 per cent. of iron, 2·5 to 3·5 per cent. of carbon, and of silicon, sulphur, phosphorus, manganese and other impurities in widely varying quantities. The composition and properties of the slag depend on the quality of the iron made.

ANALYSES OF BLAST FURNACE SLAGS.

—	1.	2.	3.	4.
Silica (SiO_2)	29·81	42·23	40·88	34·58
Alumina (Al_2O_3)	19·94	9·84	8·42	14·67
Lime (CaO)	40·31	37·13	27·46	42·88
Magnesia (MgO)	2·95	1·32	9·83	1·82
Manganous Oxide (MnO)	trace	0·97	9·74	1·40
Ferrous Oxide (FeO) ..	trace	2·60	1·57	1·23
Calcium Sulphide (CaS) ..	6·92	4·32		

1. Soft grey foundry iron. Turner, *Journ. Soc. Chem. Industry*, November 30, 1905.

2. White iron. Boudouard, *Journ. I. and S. Inst.*, 1905, Vol. I., p. 377.

3. From charcoal fired blast furnace. Shoffel, abstract in *Journ. I. and S. Inst.*, 1905, Vol. I., p. 672.

4. Edgar Thompson Furnaces, Pittsburg, U.S.A., making grey iron relatively low in silicon. Turner, "Metallurgy of Iron," p. 227.

ANALYSES OF WASTE GASES.

—	1.	2.	3.	4.
Carbon Monoxide (CO) ..	27.97	28.71	25.84	25
Carbon dioxide (CO_2) ..	10.83	10.85	9.37	12
Methane (CH_4)	—	—	0.54	2
Hydrogen (H)	1.28	1.27	2.96	2
Nitrogen (N)	59.92	59.17	56.00	59

1 and 2. From the same Cleveland blast furnace working under similar conditions, except that in case of analysis 1 the blast was heated to $990^{\circ}F$ ($532^{\circ}C$) in pipe stoves, and in the case of analysis 2 was heated to $1400^{\circ}F$ ($760^{\circ}C$) in Cowper stoves. Stead and Hawdon, *Journ. I. and S. Inst.*, 1883, Vol. I., p. 114.

3. Lürmann, Stahl u. Eisen, Vol. XXI., 1154—1155, and *Journ. I. and S. Inst.*, 1902, Vol. I., 532.

4. Typical of gas from coke fired blast furnace. Turner, "Metallurgy of Iron," p. 186.

CHAPTER III

PROPERTIES OF CAST IRON

CAST iron may be considered to be an impure alloy of iron and carbon, and its properties depend mainly on the amount of carbon present and on the condition in which it exists. The carbon may be present in cast iron in one or more of three forms, viz., as graphite (free carbon), as carbide of iron (Fe_3C), and in a state of solid solution. In pig iron and unchilled cast iron practically none of the carbon is in solid solution and all of it is found as graphite and carbide of iron. The amount of carbon present in cast iron depends chiefly upon the conditions, such as composition of the charge and temperature of the hearth, which obtain in the blast furnace during its manufacture. The condition of carbon in cast iron is determined principally by two factors, the rate of cooling and the amount and kind of impurities. Generally speaking, slow cooling favours the production of graphite and quick cooling tends to keep the carbon in the combined state, but usually the influence of the impurities is more powerful.

When cast iron contains all or almost all of its carbon in the form of carbide of iron it is intensely hard, very brittle and breaks with a white crystalline fracture. On the other hand, if most of the carbon is present as graphite the fracture passes mainly through the flakes or crystals of graphite and is grey, and the iron is soft and relatively tough. Between these two extremes we have an iron with roughly half (or sometimes nearly two-thirds) of its carbon as graphite and the rest as carbide of iron, giving a fracture which has a mottled (grey and white) appearance. Cast irons can thus be roughly classified as grey, mottled and white irons, but the very distinct variations in the fracture, particularly amongst the grey irons, allow of a very much closer classification than this.

Grading of Pig Iron.—The grading or classification of pig iron by fracture is the method almost universally adopted. The systems of grading adopted vary in different countries and in different districts, but one of the commonest systems in this country is the following.

No. 1 ; No. 2 ; No. 3 ; No. 4, foundry ; No. 4, forge ; mottled and white.

In other systems the grades are numbered from 1 to 8, and in many cases intermediate grades are recognised for foundry and forge irons.

In all systems the lowest numbers are given to the softest and greyest irons with the most open fracture, and the amount of graphite decreases and the amount of combined carbon increases as the number of the grade rises, the percentage of silicon decreasing and that of sulphur increasing. With long experience the iron at the pig bed may be graded with surprising regularity, and the suitability of the iron for particular purposes judged with great accuracy. It is, however, becoming more and more generally recognised that systematic chemical and other tests are also necessary in the proper selection of pig iron for any purpose, and such tests are commonly made and insisted upon by users.

It must be remembered that successful grading by fracture depends largely upon uniform smelting and casting conditions, which, as it happens, are usually consistently maintained in blast furnace practice. In some works, principally in America, the iron is cast in chill moulds in special pig casting machines, and under such conditions ordinary grading by fracture is impossible, the iron being selected almost solely on chemical analysis. Numerous attempts have been made to bring about the replacement of grading by fracture by grading by chemical analysis, but so far with only partial success. This result is no doubt due in a great measure to a reliance upon incomplete or inaccurate analyses, and to our as yet by no means complete knowledge of the influence of all the elements present in cast iron. There is also an opinion firmly held by many foundrymen and others that cast iron possesses a quality of "body,"

which is incapable of control by means of chemical composition or ordinary physical conditions. Difficulties of this kind will probably disappear with fuller knowledge of the constitution of cast iron, but for the present, at any rate, grading by fracture on the results of years of experience does not seem likely to be altogether superseded.

The Effect of Impurities on the Properties of Cast Iron.—It has been pointed out above that the character of cast iron depends very largely on the percentages of graphite and combined carbon in the metal, and that these quantities are, to a great extent, dependent on the amount and kind of impurities present. The impurities in cast iron, in addition, may have a distinct effect on the properties of the iron apart from their influence on the amount or condition of the carbon.

The impurities commonly present in cast iron are silicon, sulphur, phosphorus, and manganese, of which the first two vary progressively in the different grades of the same brand of iron and the last two are usually fairly constant in all irons of the same brand. The general effect of silicon is to favour the production of a grey iron by assisting the carbon to separate as graphite instead of remaining combined with the iron. Practically all white irons contain less than 1 per cent. of silicon, usually about 0·5 per cent. and sometimes as little as 0·25 per cent. On melting white iron in which other impurities are present in normal amounts, and adding silicon in gradually increasing quantities, the iron will become mottled and eventually grey. A grey iron is seldom made with less than 1 per cent. of silicon and usually contains 1·5 per cent. or more, a No. 1 iron made with hot blast having, as a rule, 2·5 to 3·5 per cent. Iron containing more than 3·5 per cent. of silicon can be readily made in the blast furnace, and silicious foundry irons containing up to 4·5 per cent. of silicon are common, while special pig iron known as ferrosilicon containing usually from 10 to 15 per cent. of silicon is made for special purposes.

It must also be noted that the total amount of carbon present in pig iron is influenced by the amount of silicon

present. Generally the higher the silicon, the smaller is the amount of total carbon present. Thus in silicious irons with about 4 per cent. of silicon the total carbon is generally less than 3 per cent., and in a ferrosilicon with 10—12 per cent. of silicon the total carbon is less than 2 per cent.

Sulphur is present in cast iron in relatively small amounts, but its effect on the properties of the iron is very pronounced. The separation of graphite is prevented or hindered by the action of sulphur, and the stability of the carbide formed is increased. The effects of silicon and sulphur are thus opposite in character, silicon tending to give a soft, grey iron and sulphur a hard, white iron.

The relative proportions of silicon and sulphur, which determine to a large extent the grade of the iron produced, are chiefly dependent on the smelting conditions. Thus a high temperature in the furnace and a limey slag favour the reduction of silicon and the elimination of sulphur. The effect of sulphur is modified by the presence of manganese, since sulphur combines with this metal more readily than with iron, and manganese sulphide has far less influence than iron sulphide on the properties of cast iron.

Manganese in itself increases the stability of carbide of iron and so has a hardening effect. It is present in appreciable quantities in most pig irons, but usually its influence on the condition of the carbon is subordinate to that of silicon and sulphur. It must not, however, be imagined that it is an unimportant constituent, although it has not so pronounced or obvious an effect as either silicon or sulphur.

In the case of pig iron for foundry purposes some manganese seems to be necessary in order to give a soft iron,* doubtless principally on account of its power to neutralise the hardening effect of sulphur, but even when only a trace of sulphur is present a cast iron with, say, 0.5 per cent. of manganese is greyer and softer than one in which manganese is absent. It is due largely to their percentage of manganese that Scotch

* This fact has been brought out recently in a paper by Turner and Hague (*Journ. I. and S. Inst.*, 1910, Vol. II., 72) in which it is shown that cast bars containing no manganese are still white although containing upwards of 1 per cent. of silicon.

irons are valued for their softening qualities when added to mixtures carrying much hard scrap. Beyond a certain amount—usually about $1\frac{1}{2}$ per cent.—the hardening effect of manganese begins to be apparent, and 1 per cent. would seem to be the limit beyond which a further increase in the proportion of manganese leads to a deterioration in the quality of the castings. In the smelting operations in the blast furnace manganese favours the removal of sulphur, and pig iron rich in manganese can be made low both in sulphur and silicon, as in the case of pig iron for the basic Bessemer process.

Phosphorus appears to have but little influence on the condition of the carbon in cast iron. It exists in cast iron in the form of phosphide of iron Fe_3P , which gives rise to a comparatively fusible constituent, the phosphide eutectic, having a M.P. of $950^{\circ}C$. This phosphide eutectic is a hard, brittle substance which, being the last portion of the iron to solidify, tends to form a network enclosing the previously formed crystals. In a cast iron which does not contain more than about 1 per cent. of phosphorus this network is incomplete and the phosphide eutectic exists in more or less completely isolated masses. Under these circumstances the strength of the iron is not seriously impaired and may in some respects be improved by the presence of the small uniformly distributed granules of the hard substance due to a moderate amount of phosphorus. As the percentage of phosphorus is increased in an iron the phosphide eutectic tends more and more to form a continuous hard and brittle network, and above about 1 per cent. its embrittling effect becomes marked.

Phosphorus increases the fusibility and to some extent makes the iron more fluid when molten. For this reason common pig iron with between 1 and 2 per cent. of phosphorus may with advantage be used for castings of plain or intricate designs in which a good surface and low cost are more to be desired than strength. Although phosphorus does not have much effect in determining the condition of the carbon, the presence of the phosphide eutectic—a white substance—causes a phosphoric grey iron to have a fracture lighter in colour than a corresponding non-phosphoric iron.

IRON AND STEEL

PIG IRON ANALYSES.*

EAST COAST HÆMATITE.

—	No. 1.	No. 2.	No. 3.	Forge.
	Per cent.	Per cent.	Per cent.	Per cent.
Graphite	3.50	3.30	3.05	2.60
Combined carbon ..	0.15	0.30	0.45	0.80
Silicon	2.75	2.50	2.30	2.00
Sulphur	0.03	0.05	0.07	0.10
Phosphorus	0.05	0.05	0.05	0.05
Manganese	1.03	1.25	1.00	0.80

SCOTCH PIG IRON (GLENGARNOCK).

—	No. 1.	No. 2.	No. 3.	No. 3, Hard.
Graphite	3.50	3.25	3.25	3.10
Combined carbon ..	0.20	0.25	0.30	0.35
Silicon	3.50	3.00	2.50	2.00
Sulphur	0.04	0.04	0.05	0.06
Phosphorus	0.60	0.60	0.60	0.60
Manganese	1.30	1.25	1.25	1.20

NORTHAMPTONSHIRE PIG IRON (THOMAS BUTLIN AND CO.,
WELLINGBOROUGH).

—	No. 1.	No. 2.	No. 3.	No. 4.	Mottled.
Graphite	3.790	3.190	3.223	3.229	1.166
Combined carbon ..	trace	trace	0.131	0.207	1.179
Silicon	2.80	1.980	1.780	1.726	1.660
Sulphur	0.006	0.010	0.018	0.020	0.168
Phosphorus	1.662	1.672	1.600	1.584	1.648
Manganese	0.360	0.360	0.398	0.216	0.216

STAFFS: COLD-BLAST CYLINDER PIG IRON (M. AND W. GRAZEBROOK).

Graphite	2.60 per cent.
Combined carbon ..	0.50 ..
Silicon	1.00 ..
Sulphur	0.08 ..
Phosphorus	0.47 ..
Manganese	0.50 ..

* Bauerman, *Journ. I. and S. Inst.*, 1908, Vol. III., p. 336.

STAFFORDSHIRE. "ALL-MINE" FOUNDRY PIG IRON (DARLASTON).

—	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	No. 6.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Graphite	3·490	3·270	3·435	3·390	2·870	2·335
Combined carbon ..	0·045	0·355	0·365	0·050	0·365	0·910
Silicon	3·360	2·847	2·586	2·613	2·269	1·605
Sulphur	0·022	0·033	0·040	0·113	0·113	0·218
Phosphorus	0·335	0·313	0·325	0·390	0·433	0·353
Manganese	0·490	0·804	0·677	0·490	0·345	0·403

CHAPTER IV

FOUNDRY PRACTICE

ALTHOUGH the greater part of the iron made in the blast furnace is converted into steel or wrought iron, a large quantity is used for the production of castings. In some works castings are made from fluid metal taken direct from the blast furnace, but this is not a common practice, and nearly always the pig iron is remelted. One grade or a mixture of two or more grades of one brand of pig iron cannot often be used except for special purposes, and it is usual to mix irons of different brands in order to obtain castings of satisfactory character.

The work of the foundry may be divided into three divisions, viz. :—

- (a) The preparation of the mould.
- (b) The mixing and melting of the metal.
- (c) The pouring of the metal into the mould and the cleaning and dressing of the casting.

The Preparation of the Mould.—The most usual method is to fashion the mould in sand, using generally a wooden pattern of the article required. In other cases the mould may be built up in loam with the aid of patterns and templates.

A great deal of the success of the ironfounder depends on his facilities for obtaining the most suitable sand or mixtures of sands for his moulds. A moulding sand must be sufficiently plastic when moistened to retain perfectly the shape due to the pattern or the tools of the moulder, and at the same time must be highly refractory in order to withstand the heat of the molten iron without any sign of fusion. The sand must also be of such a character and texture as to be sufficiently porous to allow of the ready escape of gases from the interior ; it must be in a fairly fine state of division in order to give a

good surface and take a sharp impression, but it must not be so finely ground as to reduce the porosity to a dangerous extent. Besides silica, of which they are principally composed, moulding sands contain also alumina, magnesia, lime, ferric oxide, and small quantities of other oxides. There is present also water as moisture and as combined water, the former being driven off, at least from the surface of drysand moulds, before the metal is poured.

Moulding sands consist essentially of sand or free silica with sufficient clay or silicate of alumina to give the required plasticity and make the particles of sand bind together. Free silica is very infusible and so gives refractoriness to the sand. It has, however, no binding power, this being supplied by the alumina in the form of clay. Although giving cohesiveness to the sand, clay diminishes the porosity of the sand, and an excess of alumina must consequently be avoided. Small percentages of oxide of iron are present in all moulding sands, and although this tends to decrease the fusibility, it has the advantage (due to its existence as a rough coating on the particles of silica) of giving good binding power with small proportions of clay. Impurities such as lime, magnesia, and alkalis should be as low as possible.

The proportions of silica and alumina vary in moulding sands according to the use to which they are to be put. Thus silica is lower for small than for heavy castings, and alumina may be higher for light work. The silica usually ranges from 80 to 90 per cent. for cast iron, and somewhat higher, as a rule, for steel. The alumina usually varies from about 3 to 6 per cent., but may be higher (up to about 10 per cent.) for small castings. It is not, however, possible to decide the suitability of sand for a particular purpose merely by analysis, as the properties depend also very largely on physical condition.

Sand moulds may be made in one of two ways and are known as "Greensand" and "Drysand" moulds. Greensand moulds are made from complete patterns and are used at once without any special preparation. A drysand mould is also made wholly or partially from patterns, and the whole mould, or at least the skin of the mould, is well dried before the

metal is poured. Greensand moulds are those most generally used for ordinary work, especially for small and medium sized castings, and in cases where time is of importance. Some large castings may be made in greensand, but in deep moulds and where great pressure of metal is to be withstood the stronger drysand moulds are employed. Drysand is mostly used for heavy castings and those that require special quality and soundness, such as steam and hydraulic cylinders. They involve the extra cost of drying, but this is balanced by the superior results obtained in special work, while the actual moulding costs may be less in drysand than in greensand.

In sand moulding, that part of the mould for a depth of an inch or so in contact with the pattern is made of sand of special character called facing sand. The greater part of the mould is made from sand from the floor of the foundry and known as floor or black sand. Black sand is the accumulation of facing sands that have already been used in moulds, and before use it is passed through a $\frac{1}{2}$ inch riddle. Facing sands vary according to the purpose for which they are intended, but, generally speaking, greensand facing sand is made from new sand and black sand in varying proportions, together with a certain amount of coal dust, the whole being thoroughly well mixed and passed through a $\frac{1}{4}$ or $\frac{1}{8}$ inch mesh riddle. The coal dust is added in order to prevent the sand sticking to the casting and to assist venting. Drysand facing sands must be stronger than greensand facing sands and must not be friable when dried. Sands that are too weak for use as drysand facings may be strengthened by the addition of some clay in the form of clay water.

In making moulds for steel castings the facing sand used should be more refractory than for iron, as it is required to withstand a considerably higher temperature. A silica sand containing some 95 per cent. of silica may be used, a little clay being mixed with it to give it sufficient binding power.

Cores.—Internal spaces in a casting are represented by "cores" round which the metal is cast, and the cores are broken up and removed when the casting is being dressed.

All cores are dried before being used, and when dried they must be sufficiently hard to withstand without injury the considerable amount of handling necessary in fixing them in position in the moulds. Also the cores of a mould are in most cases almost entirely surrounded by metal. They must therefore be porous enough to allow of the ready escape of gases. The sands used for cores have thus to fulfil rather more exacting conditions than the sands for the rest of the mould in that cores when dried must be strong, hard, very porous, and yet easily broken up after they have been used. Core sands should not contain too much alumina (clay), as such sands, although strong and hard when baked, are deficient in porosity, and the cores made from them are difficult to break up and remove from the casting. Binding power or cohesiveness is imparted to core sands by means of flour, rosin, core gum, or other organic binding agents, while sawdust, cow hair, or similar materials are mixed with the sand as "openers" to increase the porosity and to allow the cores to be broken up more readily for removal from the castings.

Loam Moulds.—Usually the greater part of a loam mould is built up of brickwork, strengthened with iron ties, upon which the wet loam of a thick pasty consistency is daubed and worked up to shape by hand, using templates or "streakle boards." Skeleton patterns or even complete patterns are also used in loam moulding. Articles with large curved surfaces, *e.g.*, sugar, alkali, and other pans, water pipes, etc., are those most usually cast in loam moulds, as such surfaces are conveniently formed in loam by "sweeping" them to shape with "streakle boards." The loam used must be of such a character that it will dry without cracking, and it must be strong and yet porous. A good loam may be made from some of the ordinary moulding sands, such as the Staffordshire and Erith sands, mixed with cow hair, etc., and brought to the right consistency with water or clay water. For the finishing coating to the mould a somewhat finer loam is used than is required for the rest of the mould, and the whole is carefully dried before it is used.

The patterns used for sand moulding are generally made of

wood and in two or more pieces so arranged that they can be readily removed from the sand, which is rammed round them to form the mould. If the casting is to have any hollow spaces, as in the case of pipes, cylinders, valves, and many other articles, these are occupied in the mould by sand "cores" supported by iron wire or other means. The majority of castings are made in boxes or frames, each moulding box containing part of the pattern. There are usually two boxes for each mould—the "cope" and the "drag"—which are separated from each other when all the sand has been rammed into position. The parts of the pattern are then removed, and the two boxes fitted together again in the right position, by the aid of pins and lugs fitted on the boxes. To prevent the sand in one box sticking to that in the other a thin sprinkling of parting sand (dry clean sand or burnt sand or dry crushed brick) is used between the boxes. Although only two boxes are used in the majority of cases, it is not unusual to find three or more boxes joined up to form the complete mould. Each mould has one or more suitably placed openings or "gates" through which the metal is poured, and when necessary other openings (known as "risers," "sinking heads," etc.) up which the excess of metal rises, carrying any scum or dirt, and giving a sound casting by "feeding" molten iron to those parts that might show sponginess owing to the shrinkage during solidification. The air in the mould as it is displaced by the iron escapes by the gate and the riser and also through the sand of the mould itself. The steam generated from the moisture in the sand of the mould in contact with the hot metal (especially in greensand moulds) and the gases evolved from the molten and cooling iron must also be allowed to escape. In some cases, particularly with small castings, the porosity of the sand is sufficient to allow the steam and gases to escape readily, but usually special means must be adopted, such as small holes or channels ("vents") in the sand made by an iron wire or pin.

After the pattern has been removed from the mould and any small faults have been made good by hand, a fine surface is usually given to the mould by means of blacklead or other

“blacking.” Figs. 6 and 7 are diagrams representing a plain and a cored mould respectively.

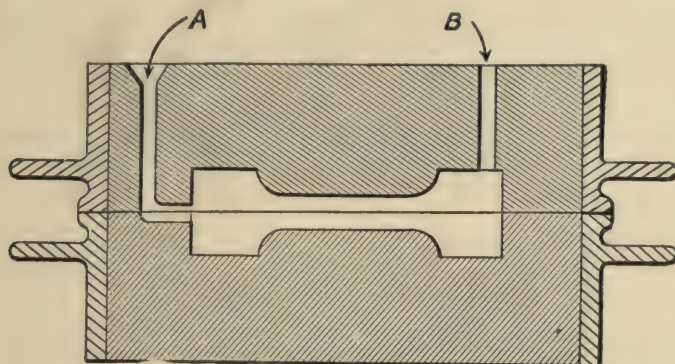


FIG. 6.—A simple mould of two boxes.

A. Gate,

B. Riser,

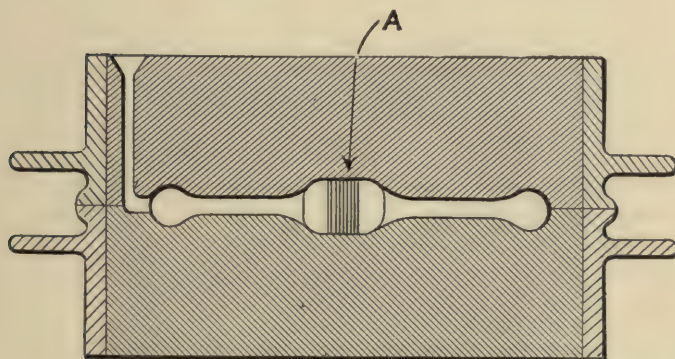


FIG. 7.—Mould of a wheel with core, A, for the centre.

Chills.—Sometimes a casting is required to have a hard surface or a surface that is hard in certain parts, *e.g.*, chilled rolls, chilled wheel treads, etc. The mould or part of the mould is then made of iron, so that the molten metal is chilled on coming into contact with the iron parts of the mould, *i.e.*, the “chills” (Fig. 8) and so remains white and hard. The iron that is used for such castings must be a close-grained strong iron which has the power of chilling or remaining white when quickly cooled, and the castings thus formed consist of a tough grey interior which

merges gradually into an outer white layer where it has come in contact with the chill of the mould. The chills must be clean and heated to a temperature of about 150°C . to dry them thoroughly before the metal is poured into the mould.

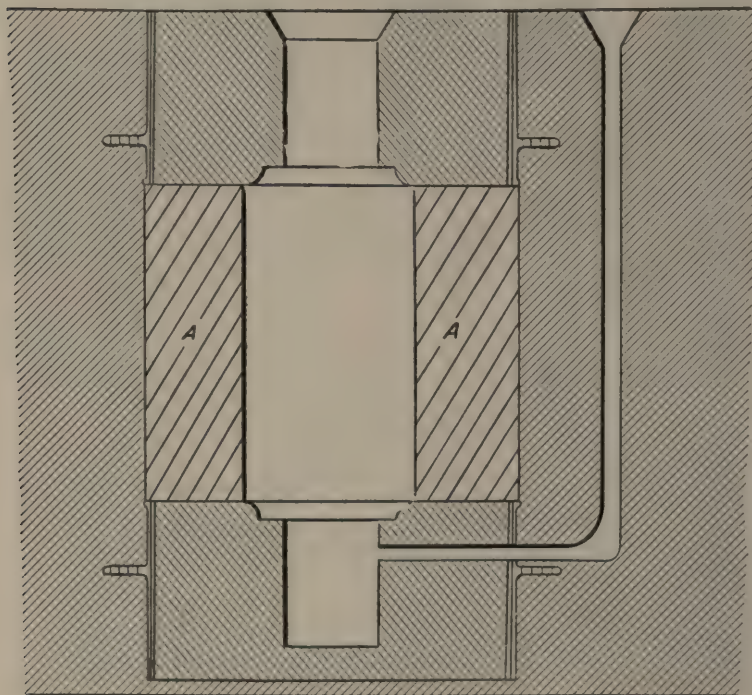


FIG. 8.—Mould showing chills *A, A*.

The Remelting of Cast Iron.—The majority of iron castings are made from metal that has been remelted in a cupola or small blast furnace specially constructed for this purpose. A reverberatory furnace known as an air furnace is also sometimes used where iron of exceptional uniformity and quality is required. Occasionally for small castings and for experimental purposes the iron is melted in clay crucibles.

Cupolas.—A cupola generally is of very simple construction

consisting of a cylindrical steel shell lined with firebrick or other refractory material, and with suitably arranged twyers for the introduction of the blast (Fig. 9). Cupolas may be classified as follows :—

(a) Solid bottom cupolas in which the bottom plate is fixed. The older forms of cupola were of this kind, which is the simplest and still often used.

(b) Drop bottom cupolas in which the bottom plate is removable, usually composed of two hinged plates meeting in the centre. At the end of the day's run the bottom is dropped, the residue (chiefly unburnt coke) is allowed to fall out, and the cupola may be readily cleaned and repaired.

(c) Cupolas with receivers. These cupolas have separate receivers or fore-hearths fixed in front of the tap-hole. The molten iron collects in the receiver and is tapped off as required, giving a better mixed, more uniform, and cleaner iron.

Apart from this general classification cupolas differ widely in details of design in other ways, principally with regard to the arrangement of twyers, whether for instance they are placed in a single row, two or more rows, or arranged spirally round and above the melting zone.

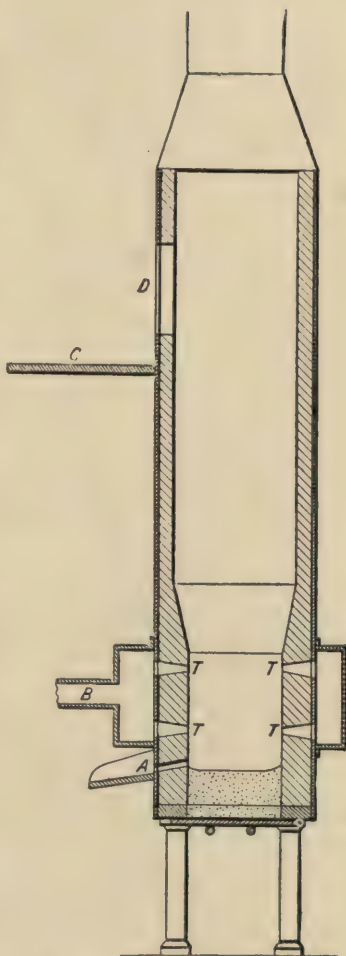


FIG. 9.—Cupola for remelting cast iron.

A. Taphole. B. Blast main.
T. Twyers. C. Charging platform.
D. Charging door.

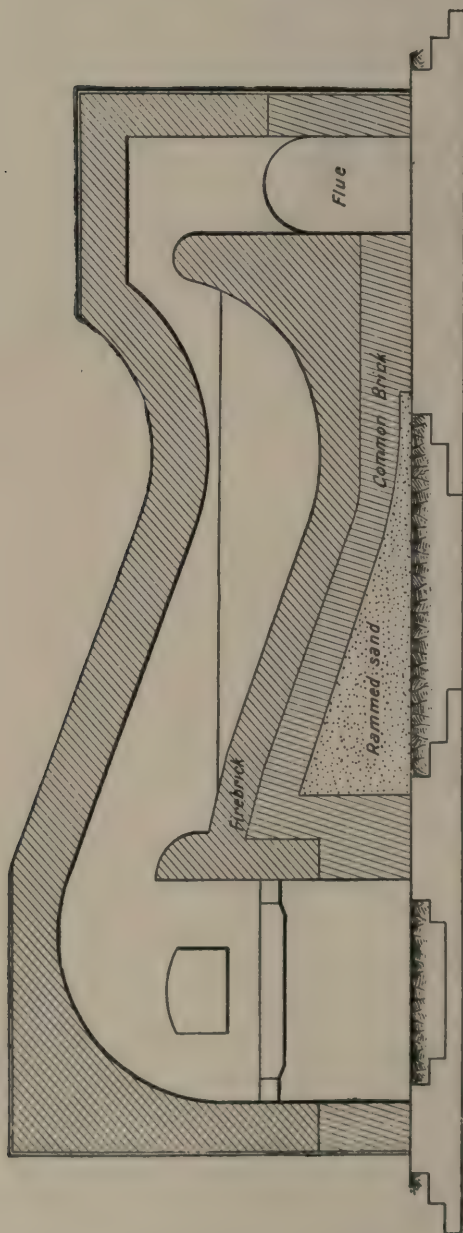


FIG. 10.—Air furnace for remelting cast iron.

The Air Furnace (Fig. 10), used for remelting cast iron, is a large reverberatory furnace of which the roof is bent downwards from the firebridge towards the flue end. This modification serves the purpose of directing the flame on to the metal, and so promotes rapid melting. The bottom of the furnace is made of sand and a reducing flame maintained, the fuel being coal. Each furnace has a capacity of several tons of metal which can be maintained in molten state until tested and additions made if necessary, although generally there is comparatively little change in composition due to remelting. The air furnace thus yields a large quantity of very uniform metal of an accurately determined quality. It is, however, costly to work as compared with the cupola, the fuel consumption being much higher and the melting slow.

CHAPTER V

MIXING CAST IRON FOR FOUNDRY WORK

THE properties of cast iron depend on the chemical composition, and also on a number of physical conditions, such as the temperature of the metal when poured, the character of the mould, and the rate of cooling after the metal has been poured. It was formerly widely believed that different brands of iron had inherent qualities, good or otherwise, quite independent of chemical composition, but, although similar views may still be heard expressed, it is now generally recognised that the source of the iron is immaterial, provided that the chemical composition and physical conditions are strictly controlled.

As the result of experience and of a knowledge of the effects of impurities, the composition of cast iron suitable for any purpose is known, and the problem resolves itself into the calculation of the necessary quantities of different brands and grades of pig iron together with, as a rule, more or less scrap cast iron, so that the whole when melted will give a cast iron of the required composition. The analyses of all the materials used should be systematically checked, and the services of a properly trained chemist are necessary if consistently good results are to be obtained. In many foundries the fracture of the pig iron, the results of personal experience, and the rules of tradition are the basis upon which mixing is carried out. Such methods, however, cannot in the long run yield entirely satisfactory results, and in most large foundries the mixing is controlled by analysis. It may be pointed out here that the method of mixing by analysis still leaves ample room for the exercise of judgment and the results of experience, as, for example, in selecting the brands of iron which are most economical under the circumstances, and most conveniently obtained.

Effect of Remelting.—The general effect of remelting on the character of cast iron is to make it harder and closer grained. The mere act of remelting causes no change in the composition or character of the iron, but in the cupola, and to a less extent in the air furnace and crucible, certain constituents of the iron are reduced in quantity owing to oxidation, while small quantities of others are absorbed from the fuel.

Turner* has shown that repeated remeltings in the air furnace result in a gradual decrease of silicon and manganese and an increase in the amount of sulphur and combined carbon. The total carbon and phosphorus are almost unaffected or very slightly increased. Changes of the same character occur when iron is remelted in the cupola, although the absorption of sulphur in the cupola, where the iron comes into actual contact with the fuel, is greater than in the air furnace, in which the iron can absorb sulphur from the furnace gases only. Generally the change in composition due to remelting in the cupola is about as follows :—

Silicon decreased by 0·4 %, *e.g.* 2·4 to 2·0 %.

Manganese decreased by 0·1 %, *e.g.* 0·6 to 0·5 %.

Sulphur increased by 0·3 %, *e.g.* 0·08 to 0·11 %.

The combined carbon increases under the influence of the alteration in the relative amounts of silicon and sulphur. The loss of silicon and manganese is due to oxidation, silica (SiO_2) and manganous oxide (MnO) being formed, which together with some oxide of iron also produced go into the slag. Usually a small quantity, say 28 lbs. per ton of iron melted, of limestone is used as part of the cupola charge in order to flux the ash of the coke and the sand and dirt attached to the pig iron.

The changes in composition due to remelting, which may vary considerably from the examples given, must be taken into account in calculating the mixture for the cupola, the probable changes being known from experience of the normal working of the cupola. In mixing irons by analysis the calculation is based principally on the percentages of silicon,

* *Journal of Chemical Society*, 1886, Vol. xliv., p. 493.

sulphur, manganese, and phosphorus required in the finished castings, due account being taken of the changes during remelting. The amount of carbon suitable for most purposes is between 3 and 3·5 per cent., which is the amount present in most brands of foundry pig iron. The question of the total carbon may thus be frequently neglected in the calculation, while the relative amounts of graphite and combined carbon are determined by the quantities of impurities present. The amount of total carbon may be increased where necessary by the use of certain brands of iron rich in carbon, *e.g.*, “Lorne” pig iron with 4 per cent. or more of carbon. In other cases a stronger and closer iron is obtained by reducing the amount of total

MECHANICAL PROPERTIES OF DIFFERENT CLASSES OF CAST IRONS.

—	Tensile Strength. Tons per sq. in.	Transverse Strength. Cwts. on 1 in. square bar, 12 ins. between supports.	Crushing Strength. Tons per sq. in.
Strong cylinder Iron	15—17	27—32	80
Fairly strong iron for general work	9—12	18—24	50
Soft, fluid iron for small and ornamental work	8—10	16—20	—

carbon by adding steel or wrought iron scrap to the charge. In most foundries more or less scrap cast iron is remelted in all mixtures. The analyses of the scrap used, which is often of variable composition, should, of course, be carefully checked, and as far as possible that used should be of similar composition to the iron which is to be cast.

Mechanical Tests for Cast Iron.—Besides the chemical test of analysis, mechanical tests of the iron should be made systematically. These include: (1) Tensile tests; (2) Transverse or bending tests; (3) Hardness tests; (4) Compression tests; (5) Shrinkage tests. For some purposes a test of the chilling properties of the iron is necessary, and occasionally torsion tests are made.

Tensile, transverse, and compression tests have been dealt

with already in Chapter I., and it only remains to say that the test pieces should be cast under conditions, such as rate of cooling, that may fairly represent those of the castings to be made from the iron tested. The size of the test piece should be standardised and cast on or in close proximity to the casting, and not in separate sand moulds or chills. The table on p. 40, shows approximately what should be obtained with different classes of irons.

For testing the hardness and homogeneity of cast iron a drilling test is frequently made, using a standard drill of usually $\frac{3}{4}$ inch diameter with a known weight (600 lbs.) acting on the point of the drill. The number of revolutions required to penetrate to a depth of 1 inch is taken as a measure of the hardness, hard or soft spots and blow-holes being also indicated by the test.

Shrinkage tests such as that devised by Keep,* or some modification of his test, should be made regularly, as they are simple to carry out and are a good check on the uniformity of work. In Keep's test for shrinkage the test bars are cast between chills, an iron yoke of J-shape being used. The distance in the gap of the yoke is 12 inches, and two bars are cast, one of $\frac{1}{2}$ inch square section and the other 1 inch by $\frac{1}{8}$ inch section. The shrinkage is measured by replacing the bars in the yokes and inserting a graduated wedge-shaped scale between the chill and one end of the bar. The amount of shrinkage depends largely on the percentage of silicon, but is also influenced by other impurities and by the casting conditions. The amount of shrinkage usually allowed for in making the pattern is $\frac{1}{8}$ inch per foot.

The Composition of Cast Iron suitable for Various Purposes.—Professor Turner in his "Lectures on Iron Founding" gives the following general relation between properties and chemical composition :—

"The maximum tensile strength is obtained with about

* A series of tests (known as Keep's tests) and referred to in detail in Turner's "Iron" were devised by W. J. Keep, of Detroit, in order to standardise a system of relative tests for cast iron, as it is practically impossible to cast test pieces which directly indicate the actual properties of the castings.

94 per cent. of metallic iron, and with the other elements in approximately the following proportions:—

Graphitic carbon	2·5
Combined carbon	0·5
Silicon	1·5
Phosphorus	0·55
Manganese	1·00
Sulphur	0·075

“Starting with this typical composition the founder can vary his mixture according to the work which may be in hand, having in view the requisite strength, fluidity, price, or other special conditions which may be necessary. In cases where the metal is required to chill, the proportion of silicon usually varies from about 0·6 to 1 per cent., the amount depending upon the depth of chill needed and the size of the casting; a lower silicon being naturally employed with larger masses of metal. If a fluid or thin iron is wanted, the silicon may be increased to about 3 or 3·5 per cent. and the phosphorus to 1·5. For such material a lower manganese is usually to be recommended, and the metal should be cast at a rather higher temperature than usual.”

F. M. Thomas in a paper * on “The Selection and Testing of Foundry Irons” gives the following notes and table on the composition of iron suitable for different purposes:—

“For thin ornamental work, such as grates, stoves, hollow-ware, or other light castings, use a mixture of No. 1 and No. 2 irons, soft and capable of taking up scrap, and with sufficient phosphorus to ensure fluidity.”

“For medium sized castings for general work, less silicon and phosphorus but rather more combined carbon is wanted. A mixture of No. 3 irons and scrap should be used.”

“For heavy machinery castings requiring strength and toughness, use irons low in phosphorus, and not too much manganese.”

“For engine cylinders and hydraulic castings, a mixture of

* Read before the Birmingham Metallurgical Society, May 9th, 1908, and published in the Proceedings.

refined or cold blast irons and scrap from a previous melt is preferable. This will give close-grained castings, tough and strong, free from undue contraction, hard and of good wearing properties, and capable of machining to a highly-finished surface."

COMPOSITION OF CAST IRON SUITABLE FOR DIFFERENT PURPOSES.

—	Thin Ornamental Work.	Medium-sized Castings for General Work.	Heavy Machinery Castings.	Engine Cylinders and Hydraulic Work.
Graphite ..	3.20 to 3.60	3.00 to 3.20	2.80 to 3.00	2.50 to 2.80
Combined carbon ..	0.08 „ 0.15	0.35 „ 0.45	0.45 „ 0.60	0.60 „ 0.75
Silicon ..	2.50 „ 2.80	2.00 „ 2.25	1.20 „ 1.50	1.00 „ 1.30
Sulphur ..	0.03 „ 0.04	0.06 „ 0.08	0.06 „ 0.08	0.08 „ 0.12
Phosphorus	1.30 „ 1.50	1.00 „ 1.30	0.40 „ 0.60	0.45 „ 0.70
Manganese	Up „ 1.00	Up „ 1.00	0.60 „ 0.85	0.50 „ 0.70

CHAPTER VI

MALLEABLE CAST IRON

MALLEABLE cast iron is made from white iron cast in the required form and subsequently strengthened and rendered ductile by a special annealing process. Ordinary cast iron, owing to its relative brittleness, is unsuitable for the production of many, especially small, articles, which owing to their intricate shape it is impossible or expensive to make by forging wrought iron or steel. By casting these articles in white iron advantage is taken of its comparatively low melting point and fluidity, and the annealing or malleablising process to which the metal is afterwards subjected yields a material with considerable ductility, high ability to resist shock, and a strength approaching that of mild steel.

Malleable cast iron is used, particularly in America, for railway work (couplers, etc.), for pipe fittings, and largely for small machinery castings, and for many small articles of thin section.

The first description of malleable cast iron and the method of its production was given by Réaumur in 1722. In Réaumur's process castings of white iron are packed in oxide of iron and heated until a portion or even the whole of the carbon is eliminated and the residue converted more or less completely into the graphitic state. Graphite in the form of flakes as it exists in ordinary grey iron causes brittleness, but when, as in malleable cast iron, it occurs in small amorphous particles of temper carbon it has no serious embrittling effect. The Réaumur process is still largely used and is the general method adopted in this country.

In America the modern "blackheart" process originated by Forquignon in 1881 is generally used. Forquignon showed that if the iron were of suitable composition malleable castings

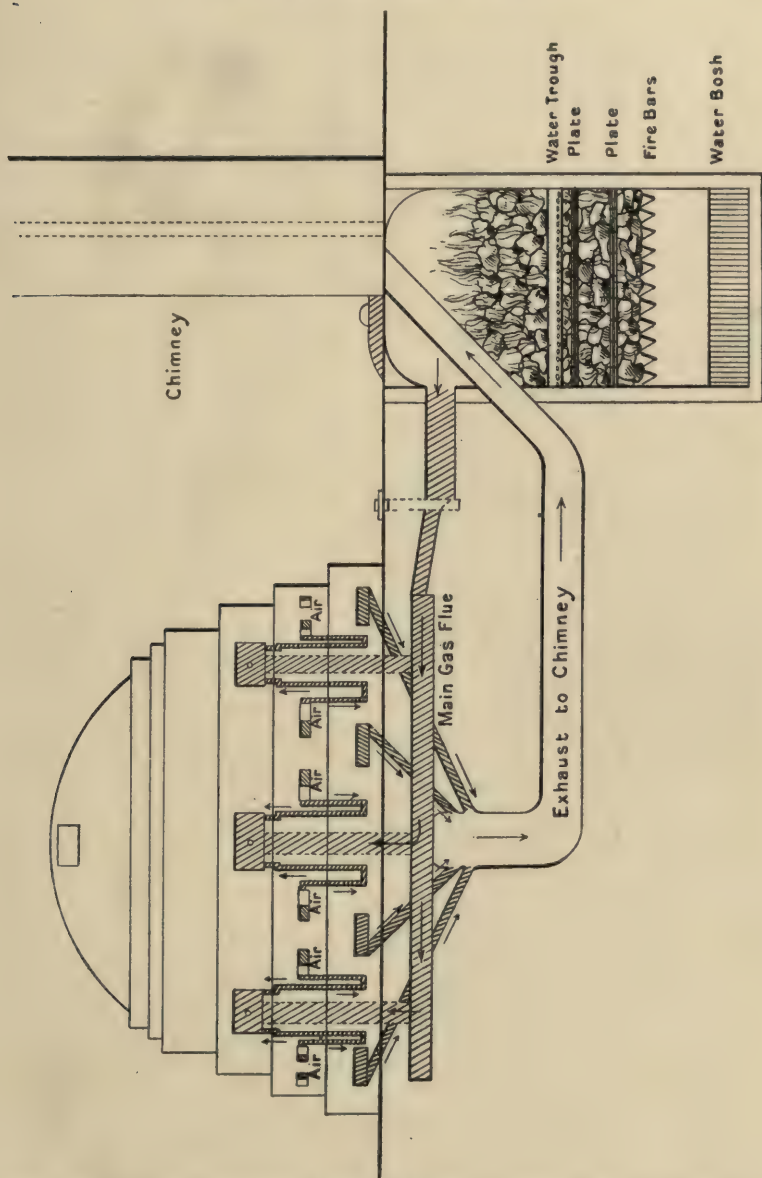


FIG. 10A.—Beehive Gas-Fired Malleable Oven (Built by Messrs. Gibbons Bros., Dudley).
Showing arrangement of air and gas flues.

could be made without elimination of the carbon by the oxidising action of ferric oxide, the castings being packed in a non-oxidising material and the whole or the greater part of the carbon converted into the graphitic form.

The Ordinary or Réaumur Process.—The iron used which is white or mottled-white is melted in an air furnace or a Siemens furnace. A cupola may also be used, and for small quantities crucible melting is suitable. The iron when cast must be hot

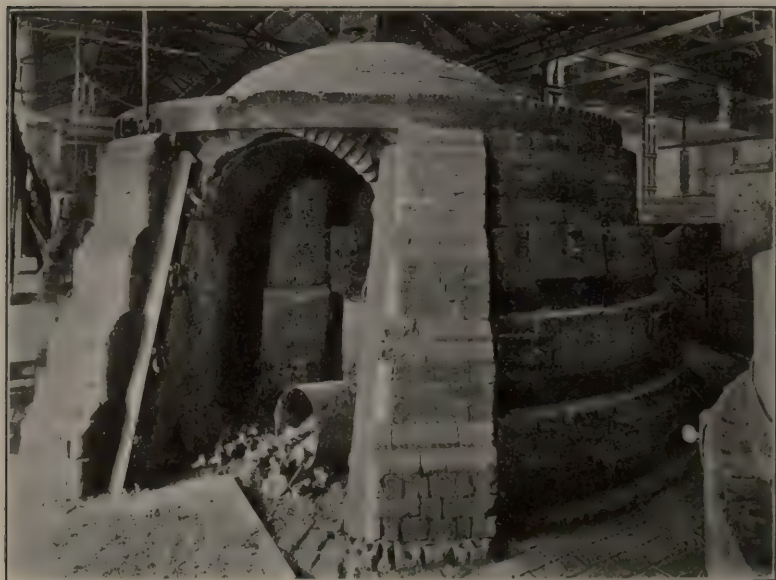


FIG. 10B.—Photograph of Gas-Fired Malleable Oven.

enough to run well in the moulds. The castings are of hard brittle white iron, and an allowance on the patterns of $\frac{1}{4}$ inch per foot must be allowed for shrinkage.* After the castings are dressed they are packed in pans or “pots” with red hæmatite iron, several parts of ore that has already been used being well mixed with one part of fresh ore. The pots are

* For “blackheart” castings an allowance of $\frac{1}{4}$ inch per foot is all that is necessary, as the deposition of the large amount of temper carbon during annealing causes an expansion.

generally circular and made of cast iron, the size for small castings being about 1 foot 6 inches in diameter and about 2 feet deep. The annealing furnace is generally of a simple type, consisting essentially of a rectangular or circular annealing chamber heated with a coal fire. Many furnaces are now gas fired, and muffle furnaces are also used.

Fig. 10a is a diagram of a modern gas-fired malleable oven showing the producer in section and the arrangement of the heating flues. Fig. 10b shows the oven in use with the door, which is built up temporarily with common bricks and moistened with black sand during the annealing operations, removed preparatory to withdrawing the pans containing the castings.

The time of annealing varies with the character of the work and depends on the size of the articles to be annealed. The oven takes usually two to three days to heat up to the required temperature, as a rule a little over 900° C., but sometimes not more than 850° C., and about the same time to cool down. Small work is maintained at the annealing temperature for 12 to 24 hours, and larger work for a proportionately longer time, sometimes as long as four days.

The cast iron used should contain about 3 per cent. of carbon, less than 1 per cent. of silicon, although some is necessary, depending on size of casting, less than 0.1 per cent. of phosphorus, and not more than 0.5 per cent. of manganese. It is not necessary to keep the sulphur low, as this is largely eliminated during the annealing, and may be present to the extent of 0.25 per cent., or even more if such iron can be cast free from blow-holes. Excess of manganese retards or may prevent the desired changes from taking place during the annealing, and phosphorus causes brittleness. The principal change brought about during the annealing is in the amount and condition of the carbon. The finished material contains usually 0.5 to 1 per cent. of free or graphitic carbon and 0.5 per cent. or less of combined carbon. The other elements, except the sulphur, which is less, remain the same as in the casting.

The "Blackheart" Process.—In this process the elimination of carbon is not attempted, or only to a minor extent, the principal

object being the conversion of the combined carbon of the white iron into temper carbon.

The process generally is similar to the Réaumur process, except that ferric oxide is not used as the packing material. Scale and less frequently bone dust, sand, and burnt clay are used, as an oxidising mixture is not necessary. The time of annealing is generally shorter, and a somewhat higher temperature is used, although a longer annealing at lower temperatures gives better results.

The iron used for "blackheart" castings may have about the same composition as for the Réaumur process, but the sulphur must be low, not more than 0.05 per cent., as none is got rid of in the annealing. After annealing the "blackheart" malleable casting contains very little combined carbon and usually some 2.5 per cent. of graphitic carbon.

The "blackheart" process is largely used in America on account of the fact that white iron low in sulphur can be obtained readily. The iron for "blackheart" castings is generally melted in either the air furnace or Siemens furnace in order to avoid the introduction of sulphur. For the Réaumur process the cupola may be used, as the quantity of sulphur absorbed is of less importance.

The mechanical properties of "blackheart" and ordinary malleable castings are not very different, although "blackheart" castings are more suitable for large articles. McWilliam and Longmuir in "General Foundry Practice" give the following as normal mechanical tests:—

—	Maximum Stress.	Elongation on 2 inches.	Reduction of Area.	Cold Bend.
Ordinary ..	18—22 tons	2½—6%	3—8%	45°—90° on ½ in. sq.
Blackheart ..	20 tons	6%	9%	180° on ½ in. sq.

A blackheart casting has a velvety or silky black fracture with a white rim, while an ordinary malleable casting has a fracture resembling a fine-grained mild steel.

CHAPTER VII

WROUGHT IRON

WROUGHT iron is almost pure carbonless iron which has been produced in a pasty condition. Since it is not melted and cast, but is the product of working a pasty spongy ball or bloom of iron mixed with a certain amount of fluid slag, it always contains in the finished state more or less of this slag in the form of elongated particles or threads intermingled with the metallic mass.

Wrought iron may be produced directly by the reduction of ore with charcoal, and in ancient times this was the only method employed. Direct methods have now been almost entirely superseded by modern indirect processes, by which wrought iron is made from cast iron produced in the blast furnace. Numerous attempts have, however, been made even in recent years to devise apparatus for the profitable production on a commercial scale of iron direct from its ores, but without any great measure of success. It may thus be stated that, except amongst primitive people and in isolated cases where special conditions prevail, direct processes are not now employed. All direct processes suffer from the inherent disadvantage of giving a small and intermittent yield of iron with the expenditure of much time and labour, and involve a larger loss of iron in the slag than is the case with modern indirect processes.

Wrought iron is now made almost entirely from cast iron by the Puddling Process which was originally introduced by Cort in 1784. Previously wrought iron was made from cast iron by refining the cast iron in contact with the fuel on hearths, using a blast to supply the air necessary for the combustion and for the oxidation of the impurities. Such methods are now rarely used except for making iron of special quality, *e.g.*,

Swedish bar iron, and the reverberatory or puddling furnace, in which the fuel is burnt in a separate fireplace, has replaced the hearths or fineries.

As originally practised the puddling process was carried out in furnaces, the bottoms of which were lined with sand which played no part in the purification of the metal, the air being the oxidising agent. Only a white iron could be used, and the process involved a preliminary treatment of the cast iron in a refinery, a grey iron being converted into a white iron by the removal of the greater part of its silicon and incidentally a portion of its phosphorus. The white iron was cast into slabs ("plate iron") and subsequently converted into wrought iron in the puddling furnaces. In the modern puddling process a furnace is used having a bottom lined with a basic and oxidising material which assists in the removal of the impurities from the grey iron melted and worked upon it.

The old puddling process is known as "dry puddling," since white iron is not very fluid when melted and not much slag is formed. On the other hand, in the modern process sometimes called "pig-boiling," the grey iron melted in the furnace is very fluid, a vigorous action or "boiling" takes place during the purification, and comparatively large quantities of a fluid slag or cinder are made.

The kind of furnace usually used for puddling is illustrated in Fig. 11. It is a small single-bedded reverberatory furnace in which the fireplace is large compared with the working chamber in order to obtain the high temperature which is necessary for the process. The furnace casing is made of suitable cast iron plates held by wrought iron tie rods, and has openings for the fire hole and working door. The sides and roof are lined with firebrick, and the cast iron plates of the bottom of the furnace support the working bottom made up of special fettling materials. The bed of the furnace is made by spreading refractory fettling—best tap (special cinder obtained from a mill furnace working with an oxide bottom), bull-dog (calcined tap cinder), etc.—over the cast iron shell to give the required thickness and shape of the bed. A fusible fettling, such as hammer slag or mill scale, is then

spread over, and this, when the furnace has been heated up sufficiently, melts and frits together the more infusible fettling

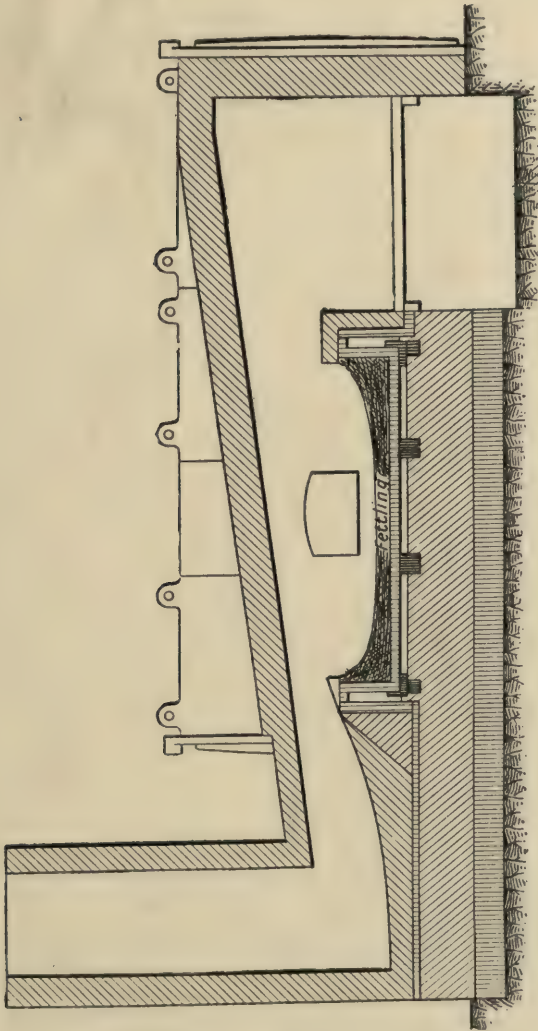


FIG. 11.—Diagram of Puddling Furnace.

into a compact working bed. The bed is finally smoothed and thoroughly consolidated by working a ball of scrap over it when the furnace is at a welding heat. The usual charge of

pig iron is about $4\frac{1}{2}$ cwts., and $\frac{1}{2}$ to 1 cwt. of hammer slag or other fusible fettling or flux is charged at the same time, in order that a fluid bath of cinder may be formed to cover the iron as it melts down. The charge takes about half an hour to melt, and during this period the greater part of the silicon, most of the manganese, and some of the phosphorus are oxidised. During the next ten minutes the iron remains in a state of quiet fusion while the rest of the silicon and manganese and a further quantity of phosphorus are removed.

At the end of this stage the iron is "cleared," and only the carbon, which so far has not been oxidised at all, and the rest of the phosphorus remain to be eliminated. The temperature of the furnace is moderated and a reducing atmosphere produced by checking the draught, the iron, which becomes less fluid, being vigorously rabbled and well mixed with the cinder. These conditions favour the oxidation of the carbon which forms carbon monoxide, the evolution of which is seen in the formation of bubbles of gas giving the appearance of boiling. During the early stages of the "boil" the evolution of the gas is violent and causes the charge to froth up. The heat is then increased somewhat and a quantity of fluid cinder is allowed to flow out over the sill of the working door into a slag waggon. This cinder or slag is known as "boilings." The evolution of gas now becomes less rapid, and bright globules of pasty and nearly decarburised iron form regularly throughout the charge, separating from the cinder, to form a spongy mass. The "boil" occupies about half an hour, at the end of which the furnace is at a good welding heat, and the sponge of iron is then worked by the puddler into balls of about 80 lbs. each. These puddle balls are withdrawn from the furnace and hammered under a steam hammer to expel much of the slag and form a bloom which is rolled into puddled bar.

In removing the impurities from cast iron they must, except perhaps in the case of sulphur, first of all be converted into oxides. Carbon is converted into carbon monoxide, which being a gas readily escapes, burns to carbon dioxide, and passes away with the furnace gases. Silicon, manganese, and phosphorus are oxidised to silica

(SiO_2), manganous oxide (MnO), and phosphorus pentoxide (P_2O_5) respectively, each of which then combines with a suitable basic or acid radicle to form a fusible compound and is removed in the slag or cinder. Sulphur can be removed to a very large extent in the puddling process, but exactly how this removal is accomplished is not clear. It seems certain, however, that little or no sulphur escapes as oxide in the furnace gases, and all of it that is removed from the iron is found as sulphide in the slag. In the modern puddling process, although some of the oxidation of impurities is due to the direct action of the oxygen in the furnace gases, it is chiefly brought about by their interaction with magnetic oxide of iron (Fe_3O_4) which is contained in the cinder and derived from the fettling. Puddling cinder consists essentially of ferrous silicates ($FeO.SiO_2$ and $2 FeO.SiO_2$) and magnetic oxide of iron. Ferrous silicates are readily fusible and act chiefly as a solvent for the magnetic oxide so far as the oxidation of impurities is concerned. The ferrous silicate of the cinder is derived principally from the hammer slag which is put into the furnace as part of the fettling and with the pig iron charged, while some is also yielded by the other fettling materials, such as bull-dog and best tap. All the more infusible fettlings consist chiefly of ferric or magnetic oxides of iron, and these provide the magnetic oxide in the cinder, ferric oxide (Fe_2O_3) when fluid being converted into magnetic oxide.

Silicon and manganese, as already explained, are removed early in the process, during the melting and clearing stages. The silicon is oxidised to silica, combines with ferrous oxide of the fettling and manganous oxide due to the oxidation of the manganese in the pig iron, and fluid silicates result. At the temperature of the puddling furnace the carbon remains unoxidised and is not removed until all the silicon has gone, and it is during the quiet clearing stage just before the "boil" that the last portions of the silicon are oxidised. As soon as this has happened the carbon is oxidised to carbon monoxide. The phosphorus is steadily removed during the melting, clearing, and boiling stages, being oxidised to phosphorus pentoxide (P_2O_5). The phosphorus pentoxide combines with ferrous

oxide of the cinder to form phosphate which remains stable in the highly basic silicates which compose the cinder. Since the oxidation of the impurities is brought about by the action of the magnetic oxide of the cinder, an equivalent amount of iron should, under suitable working conditions, be reduced, and the yield of puddled iron should be greater than the weight of pig iron charged into the furnaces. Actually, when suitable irons are used and the working carried out satisfactorily, there is such a gain in weight, but there is sometimes a loss. This loss may be due to excessive oxidation by means of atmospheric air, and in dry puddling, in which the oxidation is all of this kind, such loss is considerable. A deficiency of cinder also leads to loss of iron, as does a cinder that is too fluid, both conditions favouring the oxidation of the iron by failing to protect it from the oxidising furnace gases. Too small a quantity of cinder also results in an iron of inferior quality. It will be evident from the foregoing that a great deal of the success of the puddling process depends on having a correct quantity of cinder of the right composition, *i.e.*, containing suitable proportions of magnetic oxide and silica.

Treatment of Puddled Iron.—The masses or balls of spongy iron yielded by the puddling furnace are first “shingled,” or hammered or squeezed, in order to expel a large quantity of the fluid cinder which they contain. The appliances used for shingling are helves, steam hammers, or squeezers, of which the second are most commonly employed.

The helve, which is a primitive form of power hammer, may still be seen doing good work in forges where only comparatively small masses of iron are dealt with. It consists in its commonest form of a heavy T-shaped mass of cast iron supported at the ends of the cross piece, the end of the stem or nose being lifted by cams attached to a revolving shaft. The hammer head is fitted into the casting near the nose, and as the cam shaft revolves is lifted and allowed to fall by gravity on the puddled ball placed on an anvil block beneath. The total weight of the helve is about 6 tons, and with a drop of about 18 inches sixty blows per minute are given.

Steam hammers are now used in most works in place of helves, and for shingling purposes are usually small, 3-ton, double-acting hammers.

Squeezers are occasionally used, but their use has never been extensive, as the results are not held to be so satisfactory as those given by steam hammers or helves. By the treatment by hammering or squeezing the puddled ball is compressed, the soft particles of iron welded together, and a large proportion of the intermingled slag expelled. While still hot the mass of iron is rolled into bars of size convenient for subsequent treatment. These bars, known as puddle bars, are allowed to cool, and are then cut up into pieces of suitable length. A number of lengths of puddle bar are packed together to form a "pile." The piles of puddle bar are then heated to a welding temperature in the mill furnaces. Mill furnaces are reverberatory furnaces with a gently sloping hearth made of sand or ferric oxide, the slag or cinder due to oxidation of iron being allowed to drain to the lower end of the hearth whence it is removed. When sufficiently heated the piles are taken from the mill furnace and rolled into various sections.

CHAPTER VIII

MANUFACTURE OF STEEL

THE CEMENTATION PROCESS—CRUCIBLE STEEL

STEEL is an alloy of iron and carbon which is essentially malleable and ductile or can be forged at a red heat. The almost carbonless alloys which are made in the molten state and cast into ingots are called steel, and are in this respect distinguished from wrought iron containing perhaps as much or more carbon, but not molten when made.

Methods of Manufacture.—It is possible to produce steel of any required percentage of carbon by direct reduction of iron ores, but such methods, although the oldest, are now very rarely employed except by primitive people. Almost all steel produced at the present day is made from cast iron which is either made into steel by the Bessemer or Siemens Processes or is first purified to give wrought iron, the necessary carbon being added afterwards by the Cementation Process.

The Cementation Process.—When wrought iron is heated to a sufficiently high temperature in contact with carbon and with exclusion of air carbon is absorbed, the amount taken up depending on the length of time and the temperature of the heating. The cementation process is conducted by heating wrought iron bars packed with charcoal in closed firebrick chambers known as converting pots. Each cementation furnace consists of a pair of converting pots placed side by side. The fireplace is situated underneath the pots and the flues are so arranged as to give uniform heating. The size of the converting pots varies in different furnaces, but generally they are 8 to 15 feet long, $2\frac{1}{2}$ to 4 feet

wide, and about 3 feet deep, with a capacity of 8 to 13 tons of bars.

The wrought iron to be carburised is usually Swedish bar iron made from best Swedish white cast iron by refining by the Walloon process on Lancashire hearths. The charcoal used for cementation must be wood charcoal, and a certain proportion of old charcoal that has been used in a previous operation is mixed with the new charcoal in each charge. In packing the bars in the converting pot care is taken that no two bars are in contact, but that each is uniformly surrounded by the charcoal. When charged the pots are closed and luted up, and both covered over by an arch of wheel swarf * which is fritted by the heat of the furnace and forms a practically airtight cover. The furnace is heated up gradually during two or three days to its maximum temperature of usually 1000°C . or a little over (sometimes as high as 1100°C .) and maintained at this temperature for a period of seven to eleven days, depending on the amount of carbon it is desired to introduce. Afterwards the furnace is allowed to cool slowly during a further period of about fourteen days, the whole process taking three to four weeks.

During the cementation process the carbon enters in the outermost layers of the iron and diffuses gradually towards the centre. The carbon in the cemented bars is thus unevenly distributed from outside inwards, and in "mild heats" the bars contain a core of practically unaltered iron. The bars when withdrawn from the furnace after cementation are found to be covered with a number of smooth rounded protuberances, hence the term "Blister Steel." If the iron was of good quality and the cementation properly carried out, these blisters on the converted bars should be small and evenly distributed. The presence of these blisters is due to the action of carbon on the intermingled slag (a basic silicate of iron) in the wrought iron causing a liberation of carbon monoxide in the interior of the bar.

After withdrawal from the furnace the converted bars are

* Wheel swarf is composed of small particles of iron mixed with silicious material and is a product of the grinding of the steel for cutlery purposes.

graded according to fracture and numbered from 1 to 6,* and doubly converted bars, or No. 7, in the case of bars which have undergone two treatments in the cementation furnace. The average carbon percentage in the different grades varies with different makers, but usually No. 1 contains 0·5 per cent. of carbon and the carbon increases progressively to No. 6, which has about 1·5 per cent. of carbon. Doubly converted bars may contain as much as 2 per cent. of carbon, but beyond this amount it is impossible to increase the quantity of carbon taken up in cementation even after a number of conversions.

As has been previously pointed out, the amount of carbon in blister steel varies across the section of the bars. These bars are either cut up and melted for crucible steel, or they are heated to a red (or yellow) heat and hammered or rolled out into bars known as "plated bars" or "bar steel." Such hammered bars were formerly largely used for springs and hence were also known as "spring steel." The plated bars are broken up and six pieces piled together to form a faggot, which is heated in a hollow fire after it has been covered with a mixture of fireclay and borax to reduce as far as possible the decarburisation during the heating. When heated sufficiently the faggot is removed from the fire and welded and drawn out under the hammer to form a bar of "shear steel."

The hammered bar of single shear steel may be cut through the middle, the two halves doubled over on each other, reheated, and hammered out again to form a bar of double shear steel. Both single and double shear bars are then forged or rolled into strips which are used principally for cutlery. Shear steel is never quite homogeneous, and of course still retains a great part of the slag originally present in the bar iron, but is nevertheless a more suitable material than crucible steel when a

* The grades are also named as follows :—

- No. 1. Spring heat.
2. Country heat.
3. Single shear heat.
4. Double shear heat.
5. Steel through heat.
6. Melting heat.

cutting edge is required or when a cutting edge is to be welded to an iron back.

Crucible Steel.—In order to obtain steel of uniform composition and free, or approximately free, from intermingled slag it is necessary that it should be melted and cast. Wrought iron always contains varying but considerable amounts of slag as an essential constituent, and steel made from wrought iron bars by the cementation process followed by piling, welding, and rolling or forging still contains this slag. Also converted bars are of uneven composition with respect to carbon, and subsequent welding and working does not produce so uniform a material as is obtained by melting and casting.

The simplest and oldest method of making uniform slagless steel is by melting blister steel in crucibles or pots. This process was introduced into Sheffield in the year 1740 by Huntsman, who used fireclay crucibles. The crucibles may also be made of graphite mixed with sufficient clay to give the necessary plasticity. Such crucibles are known as plumbago or graphite pots, and are commonly used in America and on the Continent. In this country, however, fireclay pots are nearly always used, and are made, commonly by the steel makers themselves, with the utmost care from carefully selected materials. Plumbago pots, which are more expensive in the first instance, but last longer than clay pots, give up carbon to the steel, making it difficult to obtain regularly from them steel, especially mild steel, of uniform composition.

The clay mixture for crucibles, which, in Sheffield, is composed of varying proportions of different fireclays (*e.g.*, Burton, Stannington, Stourbridge) together with a little ground coke of good quality and sometimes a small quantity of kaolin, is carefully ground, and well mixed and thoroughly kneaded by treading with bare feet. Machines are sometimes used for making the crucibles, but where they are made at the works hand moulding is commonly adopted. The mould or "flask" is made of iron and has a well-fitting loose bottom. The clay is worked to shape in the mould by means of a wooden or cast iron plug having a centring pin which fits into a hole in the centre of the bottom of the flask. Both flask and plug are

well oiled, and after moulding the plug is withdrawn, the edges of the crucible trimmed, and the crucible gently forced out of the flask. The crucible is finally given its usual barrel shape by forcing in the top by means of a conical mould. The crucibles are carefully dried for several weeks and are annealed in the fire for 20 hours just before use.

Coke-fired melting furnaces of simple construction are still the kind most commonly used. Each furnace or "melting hole" consists of a chamber some 3 feet deep and of oval or rectangular section $1\frac{1}{2}$ to 2 feet square. Two crucibles previously annealed at a red heat are placed in each melting hole on firebricks or fireclay stands which rest on the firebars. Coke is packed round and the crucibles heated for about an hour. The charge is then put in through an iron funnel or charger. The lid of the pot is put on and the fire made up, and at intervals poked down and fresh coke added. When the melting is finished and the steel ready for pouring, the crucibles are taken out of the fire, the lid removed, the slag skimmed off, and the steel poured into ingot moulds. As the charge in the crucible melts more or less slag is formed, derived partly from oxidation of the iron in the charge and from rusty scrap, and also from the oxide of manganese that is frequently added in small quantities to the charge. The slag at first is basic and oxidising, but as the heating proceeds it takes up silica from the clay of the pot, and the reducing action of the carbon in the charge gradually diminishes its oxidising power. During the final stage of the process or "killing," the reducing action is sufficient to reduce manganese and even silicon from the slag. The beneficial effect of proper killing is probably due to the manganese and silicon produced in this way which enter the steel and remove dissolved oxygen and oxides. Instead of finishing the killing in the crucible, aluminium is now frequently used and less silicon obtained in the steel. There is always some loss of carbon during melting in clay crucibles, and recarburising additions, such as pure cast iron and spiegel are commonly made.

Crucible steel of the best quality is made from good blister steel which has been carefully selected in order to give

a steel of the desired composition when melted and cast. Frequently blister steel is melted with scrap, and good steel is made by melting "cut bar iron" (Swedish iron) and adding charcoal to carburise the steel to the desired degree, or pure pig iron is melted and "let down" with cut bar iron. Mild Bessemer and Siemens scrap is not used for making good crucible steel and gives inferior results when used in place of cut bar iron.

The moulds used are made of cast iron, divided into two halves longitudinally, and clamped together with rings and wedges. The ingots usually made are about 30 inches long and $2\frac{1}{2}$ inches or 3 inches square, but much larger ingots are made when required, and it is not unusual to cast ingots of crucible steel weighing many tons. For large ingots the contents of several pots are used either cast direct into the mould or into a ladle from which the steel is teemed. In any case it is essential that an unbroken stream of molten steel should enter the mould until it is full.

The ingots after removal from the mould are "topped," *i.e.*, the tops are cut off to such an extent as to ensure that the remainder is perfectly sound. Mild steel ingots have usually a tendency to rise in the moulds, but ingots of high carbon steel are "piped," *i.e.*, contain a central cavity in the top.

The ingots are very carefully reheated, being protected from oxidation on the surface by sprinkling with sand and borax, and care is taken that they are uniformly heated to the required temperature throughout. The reheated ingots are then either hammered or rolled, depending on the section and the purpose to which the steel is to be put.

CHAPTER IX

BESSEMER PROCESS

IN the Bessemer Process the impurities in cast iron are oxidised and got rid of by blowing air through the molten metal. The manganese and silicon are converted into oxides, and with some ferrous oxide which is also formed at the same

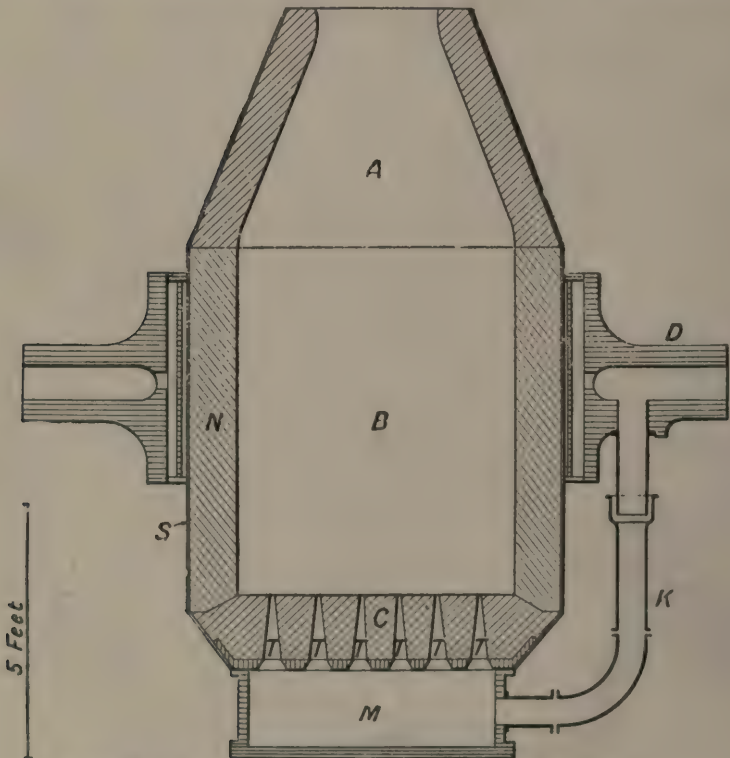


FIG. 12.—Bessemer Converter (section through trunnions).

A. Hood. B. Body. C. Bottom. T. T. Twyers. D. Hollow Trunnion.
K. Blast Pipe. M. Wind Box. N. Lining. S. Steel Shell.

time yield a fluid slag. The carbon is also oxidised in the form of carbon monoxide, which escapes and burns at the mouth of the "converter," as the vessel in which the operation is carried

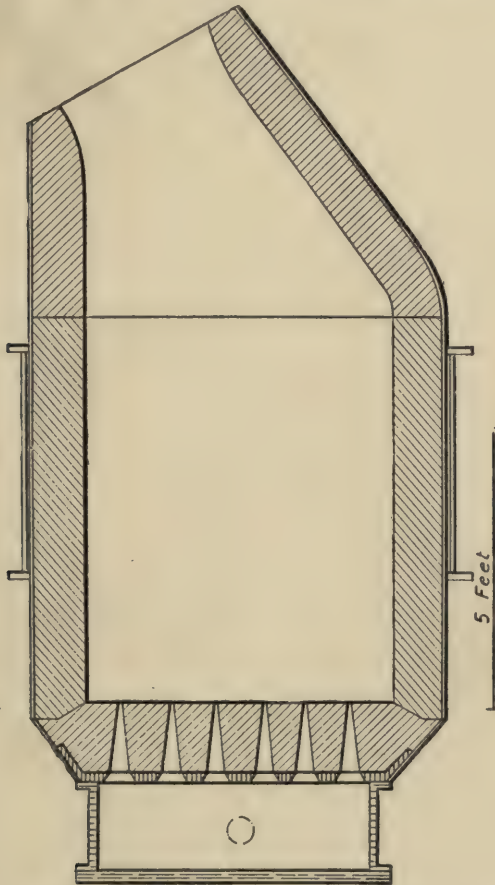


FIG. 13.—Bessemer Converter, section at right angles to trunnions.

out is called. In the early days of the process it was only possible to make steel from hæmatite iron, as phosphorus is not removed in the presence of the slag formed in a converter lined with a silicious (acid) material. Later it was found possible to oxidise and remove phosphorus in the slag by

using a converter lined with a basic material, such as burnt dolomite, and by making additions of lime to the charge during the operation. There are thus two distinct modifications (the acid and basic) of the Bessemer process, depending upon whether or not phosphorus is removed from the molten iron.

The Acid Bessemer Process.—In this process the converter shown in Figs. 12 and 13 is lined with ganister which is rammed in the bottom section round the fireclay twyers and in the body and hood between the steel shell and an inner wooden temporary liner. Ganister is a highly silicious (90 to 95 per cent. SiO_2) material containing sufficient clayey material to make it bind. With such a lining the phosphorus is not removed at all, and it is thus necessary to use specially selected iron. When the “blow” is properly conducted the carbon is not removed to any large extent until the manganese and silicon have been got rid of entirely.* The carbon is then rapidly eliminated, and it is possible, although a matter of great difficulty, to stop the blow at a point to give steel of the necessary carbon. It is, however, the almost universal practice to continue to blow air until all the carbon is eliminated, a point that is shown very definitely by the sudden diminution or “drop” of the flame of burning carbon monoxide at the mouth of the converter. The converter is then turned down, the blast shut off, and molten spiegeleisen added in sufficient quantity to give the required percentage of carbon in the finished steel and to supply the manganese necessary to ensure soundness and freedom from hot-shortness.

The cast iron used in this country is usually of the following composition :—

<i>C</i>	3—3·5 per cent.
<i>Si</i>	about 2 per cent.
<i>S</i>	less than ·05 per cent.
<i>P</i>	less than ·05 per cent.
<i>Mn</i>	about 0·5 per cent.

* In certain cases when the temperature is allowed to rise too high the carbon is oxidised completely before all the silicon is removed. In such cases of a “hot blow” the resulting steel is poor in quality. When it is found that the blow is becoming too hot and there is danger of too early elimination of carbon, it is usual to add cold scrap to cool the charge.

The iron must be added to the converter in the molten condition, and for this reason it is either melted in a cupola, taken direct from the blast furnace, or preferably taken from the blast furnace to a mixer, whence it is transferred to the converter as required.

The mixer is, as a rule, a large pear-shaped vessel, somewhat resembling a converter, and has a capacity commonly of 150 to 200 tons. It is lined with ganister or silica brick and usually gas fired. The chief advantage of using a mixer is that a supply of metal is obtained which is of uniform composition, and in some cases a certain amount of refining may be carried out in it. Thus sulphur which is not got rid of at all in the converter may be reduced in quantity in the mixer.

The Basic Bessemer Process.—This differs essentially from the acid process in the character of the converter lining, which is of basic material. Dolomite (magnesian limestone) is thoroughly calcined, or “burnt,” ground and mixed with well-boiled tar, and then rammed into position, as in the case of an acid lining. The burnt dolomite may also be used in the form of bricks, again using anhydrous tar as the binding agent. Of the basic refractory materials dolomite is the best, as, although not so cheap and readily obtainable as lime, it can be made to form a coherent lining, while magnesite, the best of all, is too expensive for profitable working. Dolomite is therefore used for the lining, and lime additions are made to the charge in the converter in order to increase the lime contents of the slag and to avoid excessive destruction of the lining. The slag in the basic Bessemer process is thus kept very limey, as by this means the phosphorus which is oxidised during the blow is converted into stable calcium phosphates (principally the tetra-basic phosphate), and hence is removed out of the iron and good steel made from phosphoric pig iron.

As in the acid process, silicon and manganese are almost or quite completely removed, while there is a considerable amount of carbon still left in the metal. The carbon is then oxidised and eliminated and the flame drops. Instead, however, of the steel being now ready for the addition of spiegeleisen or ferromanganese, it is still worthless, as it yet contains a large

proportion of its phosphorus. It is thus necessary to continue the blowing in order to oxidise and remove this impurity, lime additions being made at this stage. This final stage is known as the "after blow," the length of which is decided by the appearance of the fracture of hammered samples taken from the converter. When the phosphorus has all been removed the slag is poured off, and the addition of ferromanganese or spiegeleisen and ferrosilicon made either just before pouring the steel or when the steel is in the ladle.

The composition of a cast iron suitable* for conversion into steel by the basic Bessemer process would contain roughly—

Carbon	3·5 per cent.
Silicon	0·5 „ „
Sulphur	0·05 „ „
Phosphorus	2·5 „ „
Manganese	2·0 „ „

The slag produced contains about 14 per cent. of SiO_2 , 16 per cent. of P_2O_5 , and 45 per cent. of CaO with oxides of iron, manganese, etc. It is a valuable by-product of the process, being ground and used for agricultural purposes as manure.

* The silicon in a good basic pig should be about 0·5 per cent., but frequently the pig iron used contains considerably more (1 per cent. or over). In order to obtain low sulphur with low silicon the blast furnace charge must be made manganiferous, by adding either manganese ore or iron ore rich in manganese, and hence the high percentage of manganese in the pig iron. Irons higher in sulphur are often used, as there is usually some sulphur eliminated in the converter, while some sulphur may also be got rid of in the mixer. The percentage of phosphorus is frequently much lower (1·5 per cent. or less), but iron with high phosphorus is more satisfactory and yields a more valuable slag.

CHAPTER X

THE OPEN HEARTH PROCESS—ELECTRIC FURNACES

IN the Bessemer Process the heat necessary to keep the charge molten and raise the temperature above the melting point of steel is supplied by the rapid oxidation of manganese, silicon, and carbon, and in the Basic Bessemer Process by the oxidation of the phosphorus also. This oxidation is effected by means of air blown through the molten steel in the converter. The maintenance of such a temperature in the hearth of a reverberatory furnace is impracticable under ordinary conditions, but this difficulty is overcome in the Siemens furnace by the application of the principle of regeneration, and by the use of gaseous fuel obtained usually by treating coal in a separate furnace known as a gas producer. By the principle of regeneration is meant the transfer of the waste heat of the furnace gases to the air and gas used to heat the furnace. The gas and air are by this means separately raised to a high temperature before they enter the furnace, and an intensely hot flame results. In other words, the waste heat of the furnace gases is brought back again into the furnace and serves to increase the temperature of the flame.

The method of regeneration employed in the ordinary Siemens furnace consists in the use of two pairs of chambers filled with a chequer work of bricks of refractory material, the pairs of regenerators being used alternately to absorb the heat in the waste gases and to heat up the air and gas entering the furnace.

Referring to the diagram, Fig. 14, air and gas enter the furnace by the ports *a* and *b* and the products of combustion on their way to the chimney pass out equally through the ports *d* and *c*, giving up a large portion of their heat to the brickwork in the regenerators C and D. After an interval the supply of

air and gas through the regenerators A and B and ports *a* and *b* is shut off, and air and gas admitted through the regenerators

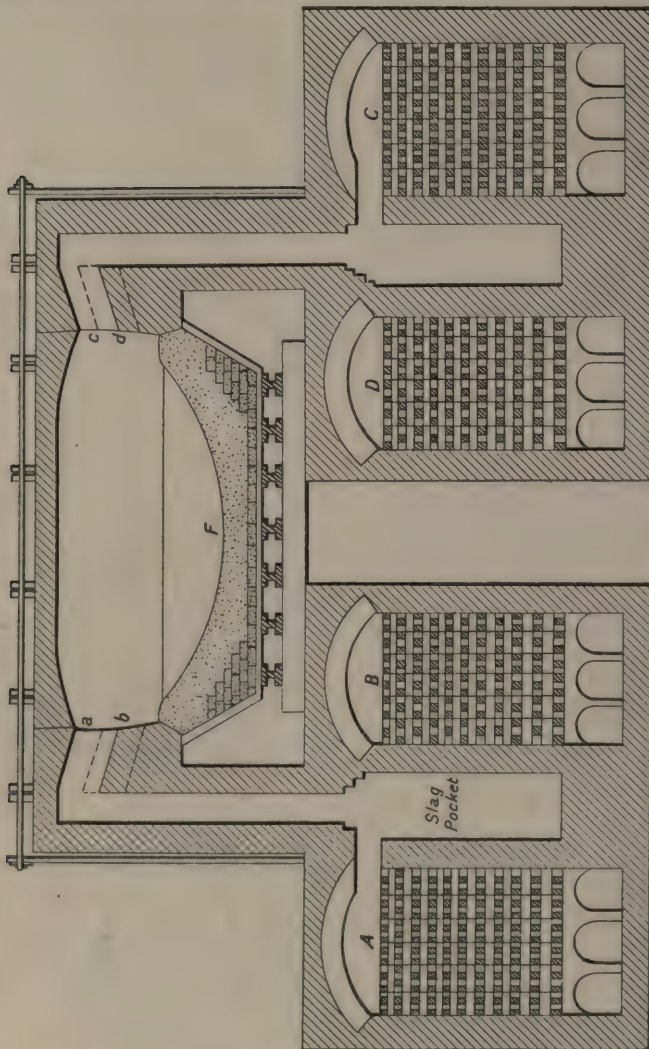


FIG. 14.—Diagram of Siemens Furnace (section through ports and regenerators).

A and *C*—Air Regenerators, *B* and *D*—Gas Regenerators.
a and *c*—Air Ports, *b* and *d*—Gas Ports.
F—Hearth.

C and *D* and ports *c* and *d*. Both air and gas are thus heated before they enter and meet in the furnace, and the waste gases are used to heat up regenerators *A* and *B*. During regular

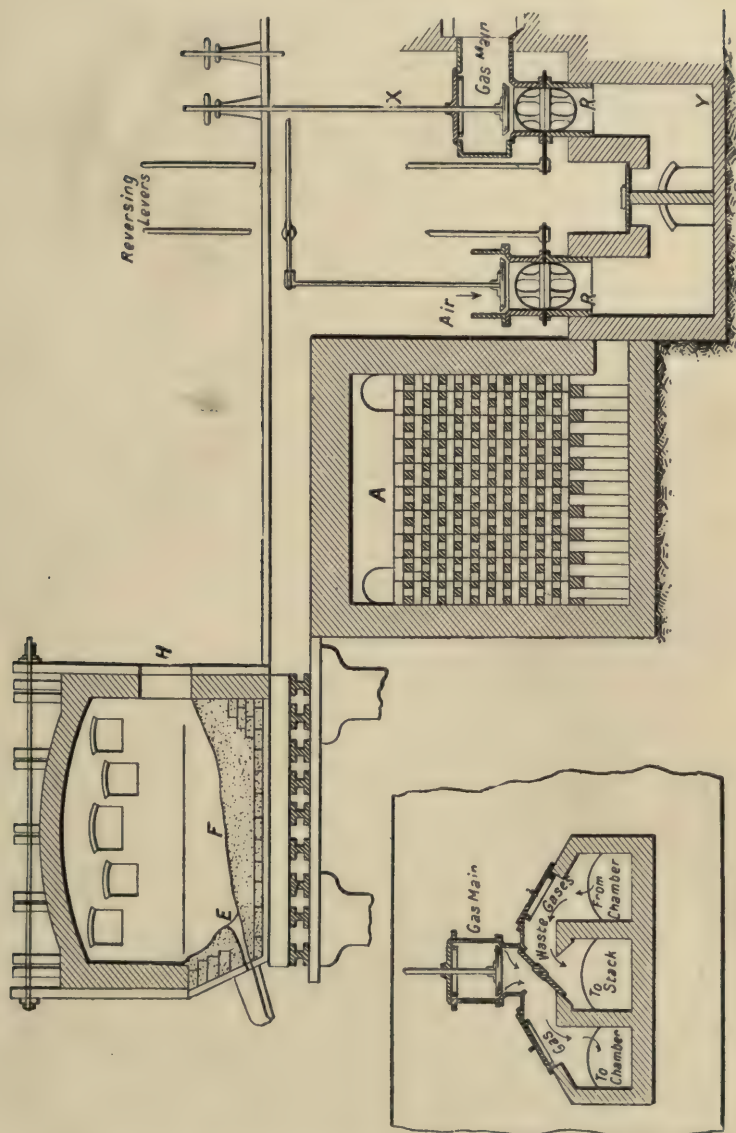


FIG. 15.—Diagram of Siemens Furnace showing Valves.

A—Regenerator.

R R—Reversing Valves.

E—Tap-hole.

F—Furnace Bottom.

H—Working Door.

working the direction of the air and gas is reversed about every 30 minutes.

A Siemens furnace consists of a chamber constructed of very refractory material, usually silica brick throughout (except the lining of the hearth), and provided with suitable ports or inlets connected with the regenerators. Reversing valves are provided to control the direction of the gas and air, and there are also valves to regulate the supply of air and the amount of gas admitted from the producers. The regenerator chambers are built at each end of the furnace chamber, which is carried separately on steel girders, and encased in steel plates, the whole being strongly supported by stays and tie rods. The bottom of the furnace rests on steel or cast iron plates carried by steel girders, and the hearth is built up with silica sand or basic material, depending on whether the acid or basic process is employed.

Two modifications of the Siemens Furnace may be mentioned here, viz., (a) "New-Form" Siemens Furnace, in which the producer and furnace are built together in one block. The hot gas is used direct from the producer and only air regenerators are provided; (b) Tilting Furnaces, in which the furnaces are supported separately on rollers or rockers, so that they may be tilted to pour slag or metal through tap-holes above the level of the metal when the furnaces are in the normal position.

The Acid Open Hearth Process.—In an acid furnace the hearth is made by heating the furnace to a very high temperature and fritting on to the bottom silica sand, layer by layer, until a suitable basin-shaped cavity is formed. The bottom and sides of the hearth are of substantial thickness, as shown in Figs. 14 and 15, and slope in all directions to the tap-hole. Since the working bottom of an acid Siemens furnace is made of silicious (acid) material it is impossible to maintain in it a basic slag, and consequently no phosphorus can be eliminated from the charge. It follows, therefore, that all the material charged (pig iron, scrap, and iron ore) must be low in phosphorus. The pig iron used must be that known as hæmatite or Bessemer and should contain not more than .05

per cent. of phosphorus. The scrap should be good quality steel scrap similar in composition to the finished steel, and the ore should be of hæmatite quality, such as red hæmatites, the red or brown Spanish ores ("Rubio," "Campanil," etc.), or good Swedish ores (*e.g.*, Gellivare ore). The following analyses may be taken to represent suitable materials:—

PIG IRON.

Silicon	2.25 per cent.
Sulphur	0.045 "
Phosphorus	0.045 "
Manganese	0.50 "
Carbon (Total)	3.50 "

SCRAP.

Silicon	0.03	"
Sulphur	0.05	" or less
Phosphorus	0.05	" "
Manganese	0.45	"
Carbon	varies	

ORE (TYPICAL OF MANY SPANISH ORES).

Ferric oxide	70.0 per cent. (49 per cent. of iron)
Silica	6.5 "
Lime	5.0 "
Magnesia	1.5 "
Phosphoric acid	0.03 "
Carbon dioxide	5.0 "
and small quantities of water, combined and as moisture, manganese oxide, etc.			

The proportions of pig iron and scrap in the charge vary in different localities. A charge consisting entirely of pig iron may be, and is, sometimes used, but more or less scrap is almost always added as part of the charge. In this country the charge usually consists of about 75 per cent. pig iron and 25 per cent. scrap. The amount of ore required varies very much according

to the charge, the kind of steel made, and the method of working. Roughly speaking, about 1 ton of ore is the amount that would be used for a 40-ton charge of mild steel, although it is possible in some cases to work a charge without any ore addition. The slag made contains about 50 per cent. of silica and about 45 per cent. of oxides of iron and manganese ($FeO + MnO$). The relative amounts of FeO and MnO vary during the process, but the two together remain nearly constant, as does also the percentage of silica, in a good slag. At the time of tapping the slag contains usually about 15 per cent. MnO and 30 per cent. FeO . Most of the oxide of iron added as ore is reduced by the carbon, and the residue combines with any excess of silica derived from the sand of the furnace hearth and so keeps the basicity of the slag constant.

The working of a charge by the acid open hearth process may be briefly described as follows. The previous charge having been tapped, the hearth of the furnace (bottom and banks) is repaired with sand where necessary and the tap-hole made up by ramming with a mixture of sand and coarsely powdered anthracite. The charge of pig iron and scrap is then put in the furnace. Usually the pig iron is charged first, and then the scrap. Many furnaces are still charged by hand, but machine charging, particularly for the larger furnaces now used, is commonly adopted. In many cases molten iron direct from the blast furnace or mixer is used. During the melting some oxidation takes place. About one-third of the manganese and silicon are oxidised and, together with some ferrous oxide also formed, are removed as slag. After melting, the oxidation of the manganese and silicon continues, and when nearly all the manganese and the greater part of the silicon have been removed, the carbon, which during the early stages is only slowly attacked, begins to oxidise rapidly, and the carbon monoxide produced rises to the surface of the bath in bubbles and gives the appearance of boiling. During the boiling stage, and previously if necessary, ore is charged into the furnace in small quantities at a time in order to promote oxidation. The iron ore (ferric oxide) reacts principally with the carbon, forming carbon monoxide, and being itself reduced to metallic iron.

When the silicon and manganese have been removed and the amount of carbon reduced to the required degree, the charge, providing the metal is sufficiently hot and the slag of a suitable character, is tapped into the ladle. Before the steel is tapped, or while it is running into the ladle, it is necessary to make certain additions to replace the manganese which has all been removed, to give soundness and toughness to the steel, and to a greater or less extent to increase the percentage of carbon. The principal "addition" in the open hearth process is rich ferromanganese containing usually about 80 per cent. of manganese. This is added in sufficient quantity to give the necessary manganese (varying as a rule from .25 to .8 per cent., according to the quality of the steel) and to combine with oxygen and dissolved oxides and with the small quantity of sulphur present. A small addition of ferrosilicon is also commonly made for the purpose of deoxidising the metal. Usually little or no additional carbon is required, as the process is stopped and the metal tapped when the carbon has been eliminated to the desired extent.

The Basic Open Hearth Process.—When a Siemens furnace is used in which the materials charged contain more phosphorus than the maximum allowable in the finished steel, the slag, as in the basic Bessemer process, must be highly basic in order that the excess of phosphorus may be removed. This condition makes it necessary that the working bottom of the furnace should be of basic or neutral material. In other respects, however, the construction of a basic furnace is the same as an acid furnace. The material almost universally used for the basic lining of the hearth is calcined (burnt) dolomite, which is usually fritted on layer by layer in a manner similar to that adopted in lining the bottom of an acid furnace.

A much wider range of materials may be used in a basic than in an acid open hearth furnace since the amount of phosphorus is practically immaterial.* The pig iron used should be low in silicon and sulphur, but the phosphorus may be present in any

* High phosphorus is not necessary as in the basic Bessemer process, since the phosphorus is not required to give heat to the metal.

amount up to about 3 per cent. The best results and most regular working are obtained with a moderate amount of phosphorus—about 1·5 per cent. or less; but pig iron with 2 or even 3 per cent. is regularly used in this country. In America large quantities of pig iron are used containing about 0·25 per cent. of phosphorus—metal very suitable for treatment by the basic open hearth process. Almost any kind of scrap steel, wrought iron, and even cast iron, low in sulphur, may be used, as, of course, high phosphorus is no disadvantage, and, when available, large quantities of scrap may be dealt with.

In working a basic open hearth charge a small amount of lime and ore is first charged into the hot furnace, then the pig iron, either cold or as molten metal from blast furnace or mixer, and afterwards the scrap, small quantities of limestone being also added during charging. If light and bulky scrap is used a portion is charged and the rest added during the melting stage. When all the charge has melted, iron ore, roll scale, basic cinder from reheating furnaces, or other suitable material rich in oxide of iron is added as required to effect the oxidation of the carbon, and lime or limestone is added from time to time to maintain a highly basic, limey slag capable of retaining the phosphoric acid formed by oxidation of the phosphorus. Since oxides of iron and lime are put in the furnace before any of the metal is charged and a highly oxidising basic slag is always present, a large proportion of the impurities may be eliminated during melting. Practically all the silicon, most of the manganese, and a large part of the phosphorus and carbon have, as a rule, been removed when the charge has melted. The remainder of the phosphorus and carbon are oxidised during the boil, care being taken that the carbon is not all removed before the phosphorus has been reduced to the required extent (·05 per cent. or less). It is very difficult, in fact often impossible, to remove all the phosphorus unless carbon is being removed at the same time, and if the carbon has all been eliminated before the phosphorus, hæmatite iron must be added in order to restart the "boil." In any case it is usual to add a small quantity of hæmatite iron just before tapping to make sure that the bath

does not go off the boil. The addition of ferromanganese, broken into small pieces, is always made in the ladle, on account of its tendency to reduce phosphoric acid in the slag and cause an increase of phosphorus in the metal. It is not possible in a basic furnace, as it is in an acid furnace, to stop the process and tap when any desired amount of carbon is present, since phosphorus is only removed with the carbon. The basic open hearth is therefore used principally for mild steel, and if additional carbon is required the suitable recarburisers must be added to the steel in the ladle.

The question of the removal of sulphur in the basic open hearth process is one of some importance. A high silicon pig iron with low sulphur is unsuitable, since the silica produced by its oxidation tends to flux and destroy the basic lining, and large amounts of lime would be necessary to keep the slag sufficiently basic. A pig iron, however, high in manganese (say 1.5 to 2.0 per cent.) can be made both low in silicon and sulphur, and such a pig iron is the one that should be made for conversion into steel in the basic open hearth furnace. Although suitable pig iron is made in large quantities, the steel maker frequently has to deal with iron containing more sulphur than can be allowed in the finished steel. In the acid furnace there is no elimination of sulphur, but in the basic furnace more or less, although an uncertain amount, is usually removed under ordinary conditions. By modifying the composition of the basic slag by the addition of dry calcium chloride, as in the Saniter process, or fluorspar, considerable reduction in the amount of sulphur can be obtained regularly. In a number of cases the iron from the blast furnace is treated by the Saniter process before going to the steel furnace. In this process lime, fluorspar, and calcium chloride are used in proportions to give a fusible mixture, which is placed at the bottom of the hot metal ladle. The heat of the molten iron fuses the mixture, which then rises and floats to the surface, removing usually about two-thirds of the sulphur. High sulphur irons are not, however, always subjected to the Saniter or other desulphurising process, and the more usual practice is to rely on the removal of excess sulphur in the metal mixer where such is in use. The

mixers commonly used in modern works are practically large tilting open hearth furnaces of several hundred tons capacity. These receive the molten metal from the blast furnace, and, besides giving a uniform product for the steel furnaces, are used for the purpose of carrying out a preliminary refining. The sulphur is removed as manganese sulphide in the basic slag present, and where sufficient manganiferous iron is used the sulphur is regularly reduced to normal amounts.

The basic open hearth process is now largely used and is increasing in importance. One of the chief reasons for this is that a wide range of materials can be successfully treated, and it is the only process capable of dealing with iron containing only moderate amounts of phosphorus. The basic process has developed very much in recent years, particularly in America, and some important modifications of plant and methods have been introduced with the object of obtaining larger and more uniform outputs. It is impossible here to describe any of these processes in detail, but mention may be made of the Bertrand-Thiel and Talbot processes. In the former the charge is partially refined and most of the phosphorus removed in one furnace (primary furnace), and then finished in a second furnace (finishing furnace), in which are lime, oxides, and scrap, at a high temperature. The charge is thus separated from the slag made in the primary furnace, and rapid elimination of the remaining impurities takes place in the finishing furnace. In the Talbot process large tilting furnaces are used and a portion of the charge poured out through the tap-hole. Fluid metal is used from the mixer and the charge worked down with oxides and lime. When finished a portion (say 40 or 50 tons from a 150-ton charge) is poured off into the ladle, ferro-manganese added, and the steel teemed in the usual way. The greater part of the slag is poured off just before the ladleful of steel, and the furnace now contains some two-thirds of its capacity of steel and some slag. Additions of oxides and limestone are made and a fresh quantity of molten metal added. The reactions occur quickly, the removal of impurities takes place rapidly, and the furnace is ready for tapping again in four or five hours. Hæmatite or low or high phosphorus metal

can be treated in these furnaces, and a large and uniform output maintained.

The Use of the Electric Furnace in the Manufacture of Iron and Steel.—The electric furnace has within the last ten years or so, assumed an increasing degree of importance in the metallurgy of iron and steel, although it is as yet not largely used in this country. At the present time its scope is confined almost exclusively to the manufacture of carbon steels and alloy steels of a special degree of purity, and to the production of ferro-alloys, being applied only to a very limited extent to the smelting of iron ores.

The many varieties of electric furnaces that have been, or are, in use practically or experimentally may be broadly classified as follows :—

1. Arc furnaces ;
2. Resistance furnaces ;
3. Induction furnaces.

In arc furnaces, such as the Stassano furnace, carbon electrodes project through the sides at a small inclination downwards. The ends of the electrodes do not come into contact with the bath, and the heating is due to radiation from the arcs. In resistance furnaces the electrodes enter through the roof and just dip into the slag of the bath, but not into the metal. The heat is supplied by the resistance of the slag and metal to the passage of the electric current and also to arcs between the electrodes and the slag. In furnaces of this kind, such as the Héroult furnace, there are no electrodes except those projecting through the roof, and the current passes through the slag and upper layers of metal between the electrodes. In other resistance furnaces, electrodes (of mild steel) are imbedded in the hearth, and the current passes from the carbon electrodes projecting through the roof through the slag and metal to the electrodes in the hearth. Induction furnaces are constructed so that the metal to be treated is contained in an annular hearth, and forms the closed secondary of a static transformer. The primary windings are connected with a high-voltage supply, and a large

low-voltage current is thus induced in the ring-shaped furnace. The resistance offered by the charge to the passage of this induced current gives the heat necessary for the melting and refining of the metal.

The principal advantages of the electric furnace for steel making, are that the metal is not exposed to contamination by furnace gases, and that, owing to the high temperatures that can be obtained, a highly basic, fluid slag can be maintained in contact with the steel. The refining and deoxidation of the steel may thus be effected to a much increased extent, the sulphur and phosphorus being both frequently reduced to 0·01 per cent. or less. The electric furnace is used for making tool steels which are said to equal the best crucible steels, although its use in Sheffield appears to have met with but little success. Steel castings of improved quality are made from steel produced in electric furnaces, and for this purpose they have proved very successful. In some cases, electric furnaces are employed in conjunction with Bessemer converters or open-hearth furnaces in order to subject the steel to a final refining operation giving a product low in sulphur and phosphorus and one more thoroughly deoxidised.

CHAPTER XI

MECHANICAL TREATMENT OF STEEL—REHEATING

THE steel made in either a Bessemer converter or an open hearth furnace is transferred to a ladle which may be slung from an overhead travelling crane or mounted on a truck running on rails over the casting pit. The molten steel is poured out of the mouth of the converter or tapped out through the tap-hole of the open hearth furnace. The casting ladle is a large cup-shaped steel vessel lined with firebrick, having in the bottom a nozzle of fireclay through which the steel is teemed into the moulds. The flow of steel through the nozzle is controlled by a fireclay stopper attached to the end of an iron rod protected by fireclay sleeves. The ingot moulds, made of cast iron of hæmatite quality, are usually open at both ends and made to taper from the bottom upwards to enable the ingot to be withdrawn. The ingot mould stands on a cast iron bottom plate (Fig. 16) and may be of any required shape and size, circular, square, oblong, oval, etc., in section, and giving ingots weighing half a ton or less up to 30 tons or more. Usually ingot moulds are rectangular in section with rounded corners. When the ingots are sufficiently solid (a few minutes after they are cast) they are stripped by lifting off the moulds by means of a crane, the crane hook being attached to the wrought iron

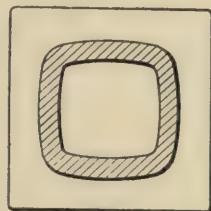
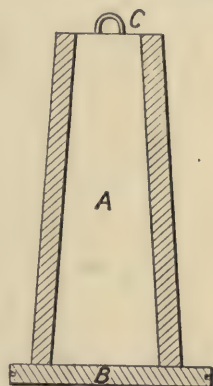


FIG. 16.

Ingot Mould and
Bottom Plate.

A—Mould.

B—Bottom Plate.

loops, *C*, cast into the top of the mould. Usually the mould and ingot separate easily, or the ingot may be made to drop out of the mould by giving the latter a few heavy blows with a sledge hammer. Frequently, however, when the moulds become worn, there is considerable sticking of the ingots with delay in stripping. To overcome this difficulty special ingot strippers are often used, and it is the practice in some modern works to place the moulds singly or two or three together on cars. When the ingots have been teemed the cars can be run out of the melting shop to a hydraulic ingot stripper by which, when necessary, the ingots can be forced out of the moulds. The method of casting on cars does away altogether with a casting pit, the cars being placed on rails on the floor level. A train of cars with their moulds is placed in position at the back of the furnace, and the steel tapped from the furnace into the ladle, which is then lifted by an overhead travelling crane and placed over the first mould. When the first ingot is cast the next mould is mechanically pushed forward under the nozzle of the ladle. The ladle is thus kept stationary during the teeming operation, and the stopper is manipulated from a platform placed at a suitable height. When the ingots have been cast, the cars are drawn out of the melting shop and the ingots stripped.

The ingots remain on the cars and are taken to the soaking pits or reheating furnaces, while the moulds are placed on other cars ready for use again. Sometimes, particularly for small ingots, moulds having closed tops are used, and the filling takes place from below. Such moulds are grouped round a central open pipe or mould to which they are connected at the bottom by means of runners.

When stripped the steel ingots are usually not solid throughout, and, even if the outside is sufficiently cooled to be in a condition for rolling, the interior is still far too hot or even fluid. To prepare the ingots for rolling or forging two methods are available. The first of these consists in allowing the ingot to cool partially or completely and then to reheat it in a special furnace until it has a uniform temperature suitable for rolling. Instead of reheating in a furnace, the ingots while still intensely

hot and fluid in the interior are placed in pits below the ground level and but little bigger than the ingots themselves. These pits, which are known as soaking pits, are lined with refractory material and are maintained at the temperature required for rolling the steel. The ingots cool slowly and uniformly in these pits by the soaking of the excess heat in the interior through to the outside of the ingot. In their original and simplest form it was necessary in starting to heat up the soaking pits by means of hot ingots which were afterwards reheated for rolling, and, when once thoroughly heated, to maintain the temperature of the pits by the soaking of a regular and continuous supply of hot ingots. It is now usual, however, where soaking pits are in use, to heat them by gas or by direct coal firing. Soaking pits of this description may thus be regarded simply as a special form of vertical reheating furnace.

Originally, in the early days of the Bessemer and Siemens processes, the ingots were reheated in coal-fired reverberatory furnaces similar to the mill furnaces used for reheating piles of puddled iron. Such furnaces, depending on chimney draught alone and requiring large furnace coal of good quality, are uneconomical, irregular in working, and cause considerable waste of steel by oxidation due to excess of air introduced through the fireplace and working doors.

Coal-fired furnaces are now constructed to burn slack and are worked with forced draught. The ashpit is closed, and the forced draught is injected by steam jets. The bed of fuel is thick, and combustion is completed by a further supply of air admitted at the firebridge, this secondary air supply being in some furnaces preheated to some extent in passages built below the furnace hearth.

Gas-fired reheating furnaces, which are now used in most steel works, are usually Siemens furnaces similar to the Siemens melting furnaces, but having a gently sloping hearth at about the level of the working doors. The hearth is also relatively large in comparison with the capacity of the regenerators, since the heat of the furnace is required to be considerably less for reheating than for melting.

The New-Form Siemens furnace (previously mentioned) is

frequently used for reheating, and is found to be very convenient and efficient for this purpose.

Many other kinds of gas-fired furnaces, in which the regenerative principle of the Siemens furnace is not used, have been built and worked successfully. In these furnaces the air for combustion is preheated in some way, such as passing it through pipes heated by the waste gases from the furnace. The producers are always built close up to the furnace, so that most of the sensible heat of the gas is available for heating purposes. The flame passes in one direction through these furnaces, and unless special means are adopted, as in the Pietzka furnace, where the position of the whole hearth can be reversed, unequal heating results. The Siemens furnace does not possess this disadvantage, as the direction of flame is reversed at intervals, and the whole contents of the furnace become uniformly heated. This fact largely accounts for the very general adoption of Siemens rather than any other form of gas-fired furnace for reheating purposes.

In the ordinary type of reheating furnace ingots or billets must either be charged cold into a hot furnace, or the furnace must be allowed to cool before the ingots are charged. The former procedure does not allow of the slow and regular heating which is necessary, especially for steels high in carbon, while the latter is wasteful in fuel. In consequence of this, continuous or inclined furnaces have been considerably developed within recent years. A continuous furnace has a long hearth, one end of which is maintained at a high temperature and the rest heated by the waste gases. The ingots are charged in at the cool end of the furnace and are either pushed along, or slide down slowly, on two water-cooled iron pipes placed in the inclined bottom of the furnace. The ingots or billets thus become slowly heated up before they reach the hot finishing end of the furnace, the bed of which is constructed in the usual manner, and all of them become uniformly heated to the same extent. Where it is required to supply regularly to the mills uniformly-sized billets or slabs, a continuous furnace can be used to advantage for the reheating, but it is not suitable for dealing with pieces of varying size. Ingots are usually

reheated in vertical reheating furnaces or taken direct from the casting pit to soaking pits. Small ingots, however, of less than about 1 ton in weight are allowed to cool and are reheated usually in horizontal furnaces, soaking pits being unsuitable. Reheating furnaces and soaking pits are lined with firebrick of good quality, and the furnace bottoms are usually made of infusible basic material such as hammer scale, hæmatite iron ore, or basic slag.*

After treatment in the soaking pit or reheating furnace the ingot is rolled or forged to the required shape. Mechanical work by forging or rolling may be put upon the metal either while it is red hot or after it has cooled down to the ordinary temperature, *i.e.*, the work may be either hot work or cold work. The effect of hot work is (1) to close up blow-holes, the surfaces of which are in most cases completely welded together at high temperatures, and (2) to give a uniform and finely crystalline structure with increase of cohesion of the crystals. Both of these actions produce increased strength and ductility. Cold work, which is carried out at the ordinary temperature, or a temperature below that at which recrystallisation can take place, causes a further increase in tensile strength and elastic limit, but causes a diminution of the ductility, especially if the amount of work is at all excessive. Steel is mostly subjected to hot working only, but is sometimes rolled or forged hot and finished cold. Cold working, besides its effect on mechanical properties, gives a better surface and a more exact finish, and also hardens the metal.

Steel cast in the form of ingots may be worked to the required shape by rolling, forging in presses, or by hammering. The object of working is not merely the production of an article of a particular shape, for of equal importance is the improvement in mechanical properties that results. It follows, then, that the effect of working should be as far as possible uniformly felt throughout the mass of the steel. The steadily applied pressure of the forging press ensures even distribution of the effect of the "work," reaching to the interior of even very large

* The use of basic slag in conjunction with old basic furnace or converter bottom was introduced by Harbord and Tucker.

ingots. The effect of hammering is confined principally to the part near the surface unless sufficiently heavy blows are given, but usually very uniformly and well worked material results. Rolling tends to draw out the outer layers of metal, and in large sections the effect of the work is much less pronounced in the interior. Rolling is the method most usually adopted and is suitable for long lengths of various sections, such as rails, angles and girders, or for plates and sheets.

The rolling mill consists essentially of a pair of cylinders, either plain or grooved, revolving in opposite directions. The space between the two rolls is of smaller area than the cross section of the piece of steel entering the rolls, and the section is thus correspondingly reduced as the piece is drawn through. For rolling plates or sheets plain rolls are used, and the rolls are screwed down closer together after each passage of the plate through them. For rolling bars, angles, rails, etc., fixed, grooved rolls are used, the grooves or "passes" gradually diminishing in size from one end of the rolls to the finishing pass at the other.

Starting with the ingot from the reheating furnace, two and often three mills are used to produce the finished section. The first and largest mill is known as the cogging mill, which reduces heavy ingots to "blooms," "slabs," or "billets," which are treated in smaller mills. "Blooms" are made when large ingots are reduced to a section of more than 6 inches square, "slabs" are similar large pieces of flat section, and "billets" are obtained when ingots are cogged down to less than 6 inches square and cut into lengths to be dealt with in small mills. From the cogging mill the steel goes to the "roughing rolls," where it is rolled approximately to the section required, and is then finished in the "finishing rolls."

The size and shape of rolls naturally vary very much according to the character of the work for which they are intended—whether for cogging large ingots into blooms or slabs, for rolling small billets, or for rolling plates or sheets, rod or wire, or rails, angles, girders, and other sections. The diameter of rolls varies from 45 to 48 inches for large cogging rolls to 10 to 12 inches or even smaller for rod or strip mills.

Rolls are usually made of cast iron, and are either "grain "

rolls or "chilled" rolls. Grain rolls are cast in dry sand or loam moulds, and are grey throughout. Chilled rolls, which are used in cases, such as sheets for tin plates, where a highly-finished surface is required, have a hard white skin on the barrel, due to casting against an iron chill. Steel rolls are also sometimes used for cogging rolls, long plate rolls, and rolls for some small sections.

A rolling mill may be "two-high" or "three-high" according to whether it has two rolls or three rolls, mounted one above the other. A two-high mill may be reversing or non-reversing. In a non-reversing two-high mill or "pull-over" mill, which is the oldest and simplest type, the steel is drawn through the rolls and then passed back over the top of the rolls, so that it only receives work in its forward journey. In a reversing mill the steel is passed in one direction through the rolls, which are then stopped and reversed, and the piece drawn backwards through the next pass, being rolled both backwards and forwards. In a three-high mill the steel is rolled between the bottom and middle rolls and then lifted and drawn back through the middle and top rolls. In the ordinary types of mills the steel is drawn entirely through the rolls before going on to the next pass, but in the "continuous" mill and "looping" mill, used chiefly for light sections, the steel enters the next pass either in a separate pair of rolls or in the same pair before the whole length of the bar is through the rolls.

Many articles owing to their size, shape, or complexity, or for other reasons, cannot conveniently be rolled. They are then worked by forging by means of presses or hammers. Steam hammers were largely used for cogging ingots before the introduction of the cogging mill, and are still used for this purpose in some small mills, and for cogging ingots for special purposes. Steam hammers are used in most cases for working the better qualities of tool steel, as a tougher and more uniform material is so obtained than by rolling. Hammers are now used generally for small and medium-sized forgings, and the modern tendency is to displace large steam hammers by hydraulic forging presses. Forging by means of the hydraulic press is the best and frequently the only method of dealing with

very large ingots such as are required for the production of large armour plates, crank and propeller shafts, etc. Steam hammers as now commonly used seldom exceed 10 to 12 tons and are usually smaller. Presses giving pressures of 2,000 or 3,000 tons are considered small, and much larger ones up to 10,000 tons are usual, and many considerably exceed this power.

Generally speaking, forging is more costly than rolling owing to the greater time, care, and labour required, but better mechanical properties can usually be got by forging. Also, almost infinite variation in size and shape can be produced by forging, whereas only standard sections can be rolled economically. Where, however, large quantities and long lengths of any particular section are required, rolling is the cheapest and best method and the most efficient.

CHAPTER XII

THE IMPURITIES IN STEEL

COMMERCIAL steel is never a perfectly pure alloy of iron and carbon, but always contains small varying proportions of other substances, all of which have a more or less marked effect upon the physical properties. The principal impurities present in steel are : Silicon, sulphur, phosphorus, manganese, and certain other substances, such as silicates and sulphides of iron and manganese, to which the name non-metallic impurities has been given. The influence of an impurity is modified to a considerable extent by the percentage of carbon present, by the amount of other impurities, by the method of manufacture, and by the treatment the steel has received.

Silicon.—The amount of silicon in properly made mild steel is usually less than 0.1 per cent., and that quantity has practically no effect on the physical properties. Considerably more silicon than this amount may be present in mild steel without any harmful effect, and in fact silicon is added up to about 0.5 per cent. in some cases, *e.g.*, in steel for castings. In high carbon steel the effect of silicon is more pronounced, but even here it is not commonly an injurious impurity.

Sulphur.—It may safely be said that sulphur, even in minute quantities, is an undesirable impurity in steel. It causes red-shortness and thus impairs the rolling qualities of the steel unless manganese is present at the same time. Although manganese minimises the effect of sulphur, the amount of the latter should not exceed 0.06 per cent. in mild steel. As much as 0.08 per cent. of sulphur may sometimes be allowed, but 0.06 is in all cases a safer maximum, and steel of the best quality should contain less. The effect of sulphur is more marked in high carbon steels, although, as these are usually made from very carefully selected material, it is not often present to the extent of more than about

0.03 or 0.04 per cent. In the absence of manganese sulphur occurs in steel as sulphide of iron, which tends to form a thin continuous network surrounding the crystals, thus causing brittleness. Also, since sulphide of iron is fluid at the ordinary rolling temperature, it gives rise to red-shortness even in small quantities. When manganese is present in sufficient quantity, however, it occurs as manganese sulphide (containing in solution more or less iron sulphide), which is much more infusible and is only plastic at the rolling temperature, while, instead of forming a network, it is present in isolated patches and is consequently comparatively harmless.

Manganese.—All commercial steels contain a certain small percentage of manganese as an essential constituent. Without manganese the sulphur and the dissolved oxides make the steel red-short, unsound, and practically worthless. The amount of manganese necessary to restore the malleability of the steel is under normal circumstances not more than 0.4 per cent. in the case of mild steel. Manganese is practically entirely eliminated in the Bessemer and open hearth processes, and the necessary amount is added at the end of the operations in the form of ferromanganese or spiegeleisen. Apart from its effect on the malleability and soundness, manganese raises the tensile strength of steel, but in amounts of 1 per cent. or more it appreciably impairs the ductility of mild steel. In mild and medium steels the amount of manganese should not exceed 0.6 per cent., although in some cases, *e.g.*, rails, 0.8 per cent. may be allowed. The effect of manganese is more marked in high carbon steels and should not exceed 0.3 or 0.4 per cent., the best carbon tool steels containing less than 0.2 per cent.

Phosphorus.—This is perhaps the most dangerous impurity in steel, as its principal effect is to cause cold-shortness and brittleness under shock. Harbord, in his Text Book on Steel, states that 0.25 per cent. of phosphorus has no effect on the rolling qualities, and such an amount would probably not affect the ordinary tensile test, although it would be sufficient to cause pronounced brittleness. Phosphorus to the extent of even 0.1 per cent. is a dangerous quantity in any steel, and for mild

steel the maximum amount should never exceed 0·06 per cent. In high carbon steel it is even more harmful, and the best tool steel should not contain more than about 0·01 per cent.

Non-Metallic Impurities.*—These include silicates of iron and manganese, sulphide of manganese and more rarely sulphide of iron, and oxide of iron. Silicates in the form of particles of slag (frequently also containing sulphide of manganese) may cause flaws and lead to fracture. In carefully made steel the quantity of included slag should be very small, but it is frequently a more serious impurity than is generally supposed.

Oxide of iron occurs in solution in iron and also in the form of minute rounded particles. It has a harmful effect on the properties of steel, particularly its power to resist corrosion, and in excessive amounts causes brittleness and unsoundness. Properly made steel should contain very little oxygen, and its presence in more than very small quantities is a sign of faulty manufacture, *i.e.*, over-oxidised metal.

The effect of sulphides has already been dealt with.

* The best description of these and investigation of their influence on steel is due to E. F. Law. *Journal Iron and Steel Institute*, 1907, II., 94.

CHAPTER XIII

THE CONSTITUTION OF THE IRON CARBON ALLOYS

THE different varieties of cast iron and steel are by far the most important and widely used alloys. A knowledge, therefore, of the constitution of the alloys of iron and carbon is not only of theoretical interest, but is a practical necessity, since such knowledge is required if the properties of any of these alloys are to be scientifically controlled. Before dealing with the alloys of iron and carbon (the constitution of which cannot yet be said to be completely and satisfactorily worked out, being still a matter of controversy), it will be of advantage to consider briefly the main principles of the subject of the constitution of alloys in general.

At the outset it must be clearly understood that all metals and all alloys are essentially crystalline when in the solid state, and no known process of quenching, annealing, or other heat treatment destroys their crystalline character. There is strong reason for believing, however, that straining a metal at the ordinary temperature (*e.g.* cold-rolling) leads to the production of a certain amount of a hard, brittle, but unstable amorphous modification round the crystals and between cleavage planes. The relative proportion of this amorphous modification is probably always extremely minute, except, perhaps, in such cases as the very thinnest gold leaf, which is semi-transparent. An alloy may consist of crystals of a single substance, or it may be a mixture of crystals of two or more substances, but in any case there are only three kinds of substances which go to make up any alloy. These three kinds of substances are :

1. Pure metals.
2. Compounds either of metals with non-metals or metals with metals.
3. Solid solutions.

Solid solutions are sometimes called "mixed crystals"—a literal translation of the German word *mischcrystall*—the term solid solution being reserved for such substances as glass. In this book, however, the term solid solution will be used, and denotes solid crystals of a substance holding one or more other substances in a state of solution. In the solid state two metals may be mutually soluble in all proportions; they may be soluble to a limited extent only, or they may be completely insoluble. In the same way metals and metallic compounds may be more or less soluble in one another.

During solidification of an alloy a pure metal, a metallic compound, or a solid solution may crystallise from the liquid, and when the alloy is completely solid further changes may and frequently do occur. Thus, pure metals or metallic compounds may undergo allotropic or polymorphic changes in the solid state, a solid solution may deposit crystals, just as crystals may be separated from ordinary aqueous solutions, or solid crystals may dissolve in a solid solution. In addition, metallic compounds may decompose or form while the solid alloy is cooled or heated. All these changes, whether during solidification or subsequently, give rise to an evolution or absorption of heat which may be large and readily noticeable, or so small as to be detected only by instruments of the greatest sensitiveness. In determining the constitution of a series of alloys a thermal examination is thus an important method of investigation and, in conjunction with the study of the microscopic structure of the alloys, generally supplies most of the information required.

The process of solidification of metals and alloys, the passage of the liquid material into a solid crystalline mass, is a definite physical change accompanied by an evolution of heat. It is not a mere gradual transition from a liquid mobile condition to a viscous and then a hard, rigid state as in the case of a glassy substance. A pure metal solidifies completely at a constant and definite temperature, the evolution of heat due to the formation of solid crystals from the liquid keeping pace with the loss of heat from the metal due to conduction and radiation. This process of solidification cannot be prevented in metals, although by cooling under favourable conditions

the commencement of the crystallisation process may be delayed, and the metal remain liquid below its true freezing point. But sooner or later crystallisation begins, and the surfused or under-cooled liquid rapidly solidifies with a rise of temperature, if the cooling is not too rapid, to the true solidifying point.

Although pure metals solidify completely at constant temperature, many alloys do not, but solidify over a more or less wide temperature interval. This is due to the fact that in such alloys solidification commences by the formation of crystals of a solid which is not of the same composition as the liquid. As soon, therefore, as the first solid particles form from the liquid alloy the remaining liquid becomes altered in composition and has a lower freezing point. At any point during the freezing of such an alloy there are present a definite quantity of a solid of a definite composition and a definite quantity of a liquid of a different but also a definite composition. Providing no heat enters or leaves the alloy no change occurs—the solid and liquid are said to be in equilibrium. If heat is abstracted from this alloy solidification proceeds and the temperature slowly falls. In the case of pure metals and certain alloys solidification begins and ends at the same temperature. In these cases solidification begins by the formation of a single solid of the same composition as the liquid, or of more than one solid, the average composition of which is the same as the liquid. Thus liquid and solid do not alter in composition during freezing, and the temperature remains constant, as heat is lost by the alloy until solidification is complete. Conversely, during melting heat is being absorbed by the alloy and all used up in producing a change in state, the temperature remaining constant during the whole time the metal or alloy is melting.

Speaking generally, in any alloy of two metals the liquid, during solidification, can exist side by side and in a state of equilibrium with not more than two separate and distinct solids, and then only while the temperature remains constant.* Also,

* It is customary in the case of alloys to neglect the consideration of the effect of pressure and to assume the absence of vapour, since most alloys are not

if during the solidification of an alloy of two metals a single solid crystallises which has not the same composition as the liquid, the temperature falls as freezing proceeds, and the solid and liquid in equilibrium with each other alter in composition as the temperature falls. Similarly, after the alloy is completely solid any further changes in constitution of the alloy proceed or tend to proceed on the same lines. That is to say that not more than three separate and distinct solids can exist in the alloy in a state of equilibrium, and then only at some definite temperature, while the alloy may consist of either one or two substances in equilibrium over a range of temperature. Each separate, distinct, or individual substance in an alloy or any other system is spoken of as "a phase." There can only be one vapour phase, as all gases are miscible in all proportions. In the case of the majority of alloys there is also only one liquid phase—in alloys of lead and tin, for instance, a molten alloy of 70 per cent. lead and 30 per cent. tin is the same phase as a molten alloy of 80 per cent. lead and 20 per cent. tin, the two liquids having no separate individualities and when in contact diffusing into each other to give a single uniform liquid. There are many examples, however, such as lead and zinc, of alloys which when molten separate into two distinct homogeneous liquid layers, and we then have to deal with two liquid phases. Each solid metal and each metallic compound that exists as a separate substance is a phase, and every allotropic or polymorphic modification of a metal or compound having a separate existence is a phase. Solid solutions are also phases, but differences in composition do not constitute different phases unless the solid solutions are capable of existing in contact with each other in a state of true equilibrium as separate, distinct, and homogeneous crystalline bodies.

By a study of the thermal changes which occur during heating and cooling, together with microscopic examination and other methods of investigation, the constitution of a series of alloys may be determined, and a diagram having temperature and

appreciably volatile under ordinary conditions, and are used and worked under atmospheric pressure. These assumptions are quite reasonable and much simplify the discussion of their constitution.

composition as ordinates constructed showing the phases that are in equilibrium (the normal constitution) in any alloy of the series at any temperature. Such diagrams are known as "Equilibrium Diagrams." Each line of the diagram indicates the conditions under which one phase appears or disappears, and a point where four lines meet marks the simultaneous appearance or disappearance of two phases. Each vertical and horizontal line marks the boundary between regions in

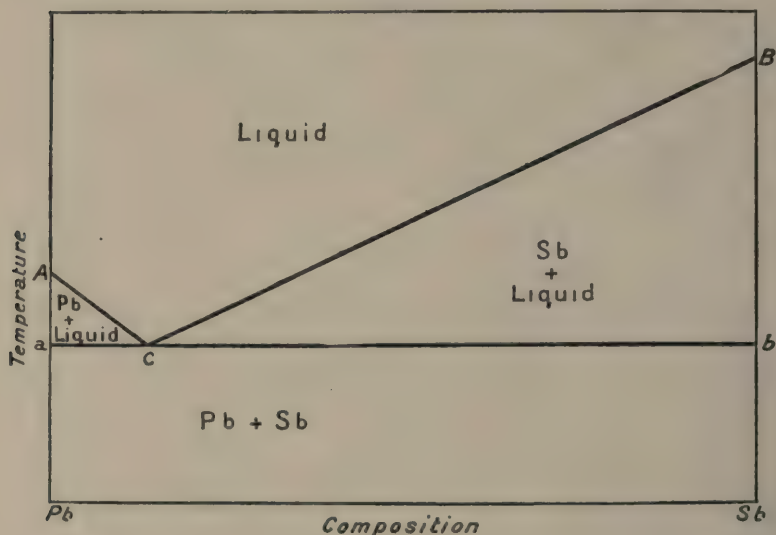


FIG. 17.

which the alloys consist of two phases in equilibrium, and sloping lines show how the limits of liquid or solid solubility change with alteration in temperature, each sloping line being the boundary between a single-phase and two-phase system.

One of the simplest types of equilibrium diagrams is that of alloys of two metals which dissolve in each other in all proportions when liquid, are quite insoluble when solid, and neither combine together to form compounds nor undergo allotropic change. As an example of this type of diagram may be taken

that (Fig. 17) representing the constitution of the alloys of lead and antimony.*

Above the two lines AC, CB the alloys are entirely liquid, and as the two metals have complete liquid solubility, there is only one liquid phase (a uniform solution of the two metals) for any alloy. The temperature at which pure lead freezes is shown by the point A. At temperatures above A lead is liquid, below A it is entirely solid. The addition of antimony to lead lowers the temperature at which freezing commences as indicated by the line AC. Similarly the freezing point of antimony is lowered by addition of lead as shown by the curve BC. Alloys containing from 0 to 13 per cent. of antimony (A to C) *commence* to freeze by separation of lead crystals, and alloys containing from 13 to 100 per cent. of antimony (C to B) *commence* to freeze by the formation of antimony crystals. The alloy containing 13 per cent. of antimony and 87 per cent. of lead, which has the lowest freezing point of all the alloys of the series, is known as the "eutectic alloy" and freezes at the temperature indicated by the point C, by the simultaneous crystallisation of lead and antimony, the temperature remaining constant until the whole is solid. As soon as the process of solidification of the eutectic begins, solid lead, solid antimony, and liquid solution of antimony and lead exist together. There are thus three phases present, and these can only remain together in equilibrium while the temperature is constant. As the system loses heat, change occurs in the relative amounts of the three phases present, but the temperature does not fall until there is a reduction in the number of phases. In this case the amount of liquid gradually becomes less and less and finally disappears. The alloy is now completely solid, there are only two phases (solid lead and solid antimony) present, and the temperature falls regularly as further heat is lost by conduction and radiation. Alloys containing more than 87 per cent. of lead (the eutectic composition) begin to freeze by the crystallisation of lead. The liquid is thus

* Lead and antimony are usually regarded as being perfectly insoluble in each other in the solid state, and certainly appear to be practically so, although it is doubtful if absolutely perfect solid insolubility exists between any two metals.

correspondingly poorer in lead and has a lower freezing point, and the temperature falls before more lead crystallises out. As lead continuously separates during this stage of the solidification, a point is eventually reached when at the temperature C the remaining liquid has the composition of the eutectic.

The residual liquid now solidifies at constant temperature C, giving a mixture of solid lead and antimony. The solid alloy thus consists of primary crystals of lead and a matrix of the eutectic. Similarly the alloys containing less than 87 per cent.

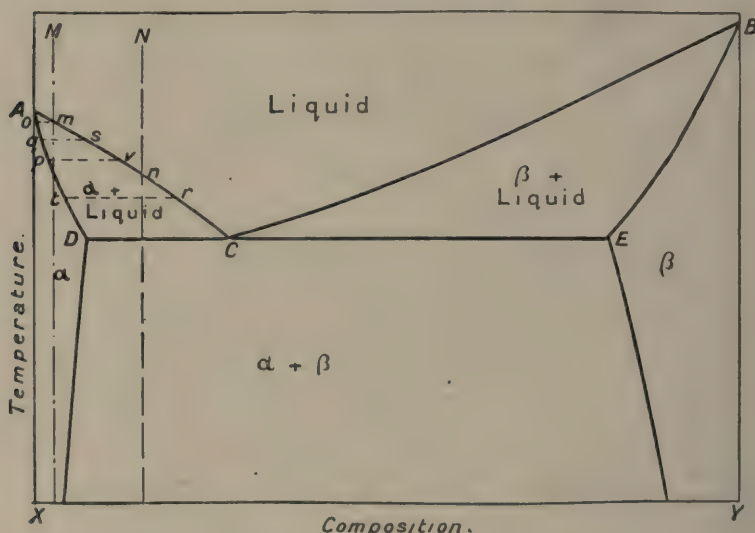


FIG. 18.

of lead begin to solidify by the crystallisation of pure antimony which continues to separate with falling temperature until the residual liquid has the eutectic composition. This residual eutectic solidifies at constant temperature (C) and the solid alloy consists of primary crystals of antimony in a matrix of eutectic. Of all the alloys of lead and antimony there is one which when solid consists of eutectic only, and all the others consist of more or less eutectic with either lead or antimony in excess. It should be remembered, however, that every solid alloy of the series consists of the same two phases, lead and antimony, and

that as regards the question of equilibrium of any system it is only the *number* of the phases present that is of importance, and not their amounts or distribution.

Complete or practically complete insolubility among metals in the solid state is rare, and solid solutions, either of metal and metal or metallic compound and metal, are of very frequent occurrence.

Fig. 18 is the equilibrium diagram of two metals, such, for example, as copper and silver, which are partially soluble in each other when solid and give an alloy of composition C (the eutectic) which has the lowest melting point of the series, the two metals also being perfectly soluble in each other when molten, and neither uniting to form a compound nor undergoing any allotropic change. Considering this case in general terms and calling the two metals X and Y, the alloy of composition M consists when solid of a uniform solid solution of Y in X which we will call α . At temperatures above the line AC the alloy is liquid. On cooling to the point m solidification begins and the solid first formed has the composition o . It is not the pure metal X, but a solid solution of Y in X of composition o . The separation of this solid alters the composition of the liquid, and the temperature falls before further solidification takes place, the solid forming also changing in composition. At any instant during the solidification, if equilibrium is maintained by means of diffusion in the solid and between solid and liquid, there exist together in equilibrium one uniform solid solution of Y in X having the composition given by the line AD and one uniform liquid solution of a composition given by the line AC. Thus, when the temperature has fallen to q the alloy consists of crystals of α of composition q in equilibrium with liquid of composition s , and just before the alloy is completely solid the crystals have the composition p and the liquid has the composition v , if equilibrium is maintained. Finally, when solidification is complete the alloy consists of crystals of a solid solution of composition M. The alloy N commences to solidify at the temperature of the point a , and solidification proceeds as in the case of alloy M until the temperature of the point C is

reached. The alloy now consists partly of crystals of solid solution α of composition D and partly of liquid of composition C. The solid is the saturated solution of Y in X while the liquid is of the composition of the eutectic. Further solidification takes place by the simultaneous formation of saturated solid solution of Y in X of composition D and saturated solid solution of X in Y of composition E. During this stage of the solidification there are thus present three

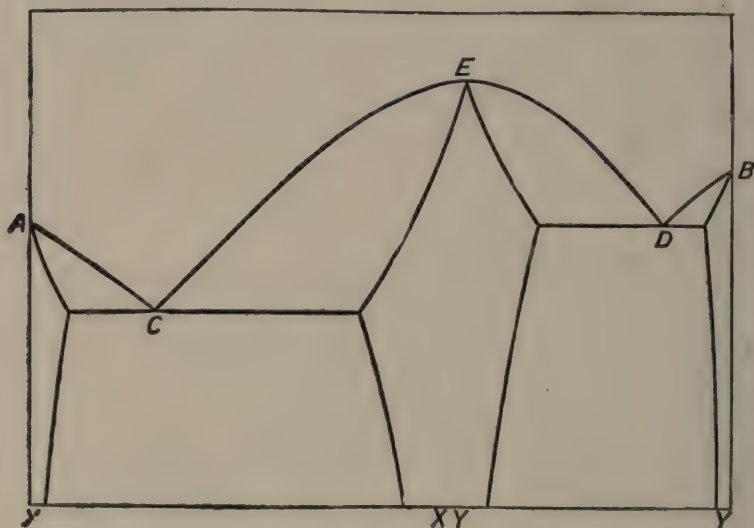


FIG. 19.

phases, the liquid and the two saturated solid solutions. The temperature now, therefore, remains constant until solidification is complete and the liquid phase has entirely disappeared. Alloys containing the metal Y in quantity in excess of that required to give the eutectic solidify in a similar manner by the formation of the solid solution (β) of X in Y and, if between compositions C and E, of eutectic as well.

It will be noticed that the compositions of the two saturated solid solutions at the temperature C are given by the points D and E, but as the temperature falls the solubility changes,

just as the solubility of salt in water varies with the temperature. The lines DF and EH mark the limits of the solid solubility of the two metals at different temperatures, and indicate that saturated α solid solution, for example, separates from saturated β solid solution as the temperature falls.

In the two typical series of alloys that have been considered the metals did not combine together to form a compound, and it now becomes necessary to deal with a simple case in

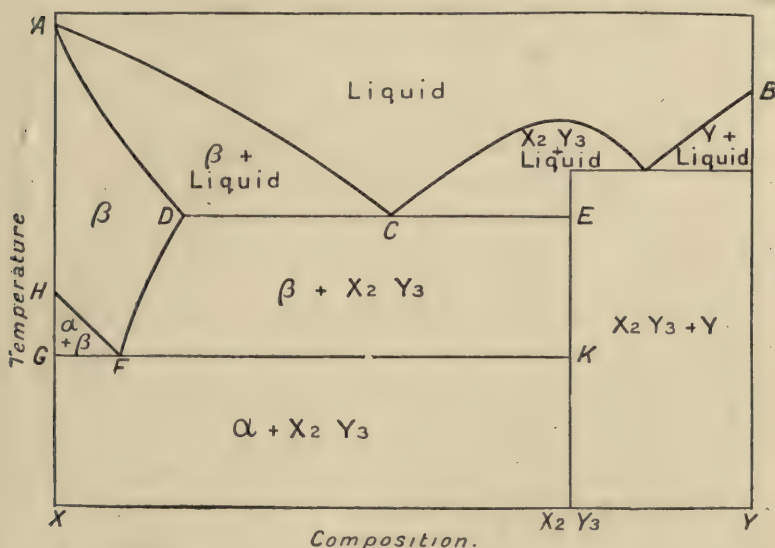


FIG. 20.

which the two metals unite chemically. If two metals unite to form a compound which melts without decomposition its melting point will constitute a maximum on the liquidus curve. Such a compound may or may not be capable of forming solid solutions with its component metals, but if it does so to a limited extent, then the equilibrium diagram may be of the kind illustrated in Fig. 19. It will be noticed that such a series contains two eutectics and may be considered as two series of alloys each like the second of the typical series already discussed.

At this stage it is convenient to deal with the changes produced in the equilibrium diagram by polymorphous transformations, such as allotropic changes in either of the component metals. Consider the ideal case represented in Fig. 20. Here the metal X exists in two allotropic modifications which may be called α and β , α being stable when the pure metal X is below the temperature H , and β stable only above the temperature H . The temperature at which the metal X passes from the β to the α condition on cooling is altered by the presence of compound X_2Y_3 in solid solution, just as the temperature at which metal X solidifies is altered by the presence of metal Y in liquid solution. This is represented by the curve HF in the diagram, from which it will be seen that the change from β to α begins at progressively lower temperatures as the amount of compound X_2Y_3 in solution increases until at temperature G the residual β of composition F breaks up into a conglomerate of α and the compound X_2Y_3 . It will be noted that it has been assumed that the α modification of the metal X is incapable of holding any of the compound X_2Y_3 in solid solution, and that the line GFK therefore extends to the left-hand boundary of the diagram. This line GFK is analogous to the eutectic line DCE , and the alloy F (known as a eutectoid) is analogous to the eutectic alloy C .

In discussing the constitution of the few typical series of alloys* which have so far been considered it has been assumed that true equilibrium has always been obtained. This, however, is by no means always the case in practice, and many alloys of great industrial importance would be of little value if brought to a condition of equilibrium. There are numerous well-known examples of substances which may be kept indefinitely without showing any sign of change, although actually in an unstable condition. Thus a supersaturated solution of sodium thiosulphate may be cooled down to the ordinary temperature and yet show no sign of crystallisation even if shaken. If, however, a minute crystal of this same sodium thiosulphate, or of an isomorphous substance, be introduced into the supersaturated

* There are several other important types, but those dealt with should enable the reader to understand the iron-carbon diagram which is given later.

liquid, crystallisation begins and goes on rapidly. The supersaturated solution of sodium thiosulphate is said to be in the metastable state, and the stable crystalline phase is only formed on the introduction of nuclei of that phase. Although when once started the change from the metastable to the stable state in many cases takes place with great rapidity, such is not always the case, and the stable form may only be produced with extreme slowness. The rapidity of the change from the metastable to the stable state is influenced in several ways. Thus the higher the temperature and the further it is from the transition point the greater is the velocity of the transformation. In the case of undercooled substances, *i.e.*, those in which a physical change has been wholly or partially suppressed during cooling, the influence of the falling temperature is, in itself, in the direction of retarding the tendency to equilibrium, and at the same time the removal from the transformation temperature increases this tendency. These two influences thus oppose each other, and during cooling a point is reached where the rate of change from the metastable to the stable phase is a maximum. Thereafter on further cooling the rate of change diminishes rapidly and at lower temperatures frequently becomes vanishingly small. Small quantities of other substances may act powerfully in accelerating or retarding the change, and, as has been shown above, under some conditions the stable phase is not formed except when nuclei of that phase are present to act as centres of crystallisation. The reluctance to form new phases, which in a greater or less degree may be said to be universal and accounts for the many examples of metastable equilibrium, is of great practical importance. In a large number of cases the object of heat treatment is either to accelerate the change from metastable to stable equilibrium or to produce conditions favourable to the retention of a metastable phase. In the case of iron-carbon alloys metastable equilibrium is of great importance, and to it in a large measure is due their wide range of usefulness.

The first equilibrium diagram of the iron-carbon alloys was constructed by Roozeboom and was based upon the work of Roberts-Austen. This diagram marks the most important

advance of modern times in this branch of the metallurgy of iron and steel, and, although since modified in some important details, is generally acknowledged to be the best expression of the constitution of these alloys. A completely satisfactory diagram has yet to be proposed, principally with respect to the relative stabilities of graphite and cementite and the consti-

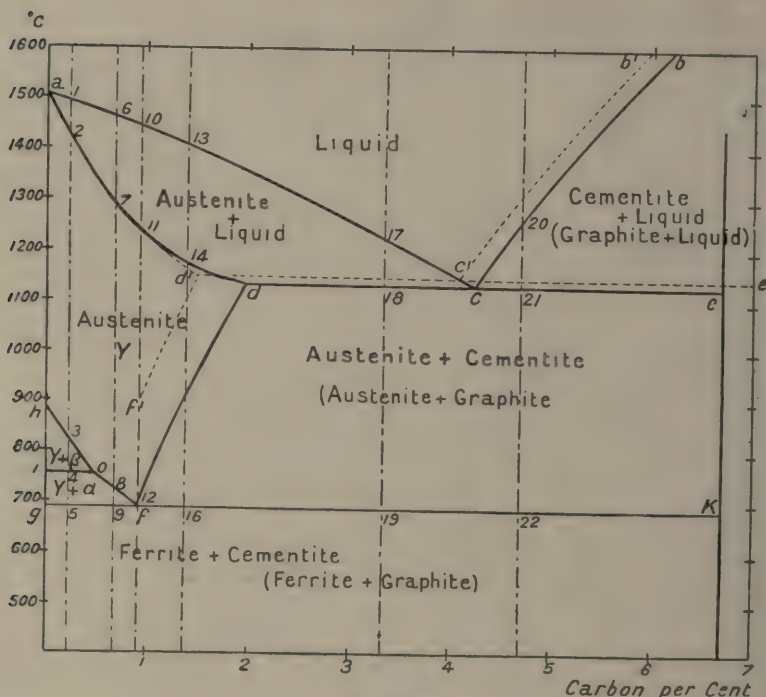


FIG. 21.

tution of the cast irons. In the Roberts-Austen and Roozeboom diagram cementite (Fe_3C) is marked as a stable phase below $1000^\circ C.$, and graphite stable above that temperature but not below. This view cannot be made to agree with many known facts, such as the production of malleable cast iron by the annealing of white iron at temperatures below $1000^\circ C.$, or the formation of grey irons by slow cooling. From such facts as these and from the results of much experimental work it is

concluded that in the solid state graphite is a stable phase at all temperatures and the carbide of iron is metastable. At the ordinary temperature ferrite and graphite are the phases in equilibrium, although this may only be obtained after very prolonged annealing. If these views are correct, it would appear that in the iron-carbon alloys we have to deal with both stable and metastable systems, and it was proposed by Heyn and others that two systems should be represented in the diagram. Such a diagram, although not completely satisfactory, probably best represents our present knowledge and is the one given here in Fig. 21. The diagram of the metastable (cementite) system is given by the full lines, while the dotted lines refer to the stable (graphite) system.

Considering first the metastable diagram, which deals with white irons and steels, it will be seen that the upper part of the diagram indicates a limited solubility of carbide of iron in iron and a eutectic of solid solution and carbide at 4.3 per cent. of carbon with a melting point of 1130°C . In the lower left-hand corner of the diagram allotropic changes in iron are indicated. Iron exists in three forms known as α , β , and γ . Below 760°C . iron exists in the α form and is known as ferrite. Carbide of iron is insoluble or practically insoluble in ferrite. At 760°C . the α -iron changes to the β modification which is non-magnetic and like α -iron incapable of dissolving carbide of iron. Above 890°C . iron exists in the γ condition and in this state is capable of holding carbide of iron in solution to a limited extent. The details of the diagram will be best understood by considering the changes that take place in a number of alloys throughout the series. Taking first mild steel with, say, 0.2 per cent. of carbon, the beginning and end of solidification is given by points (1 and 2) on the curves ac and ad . When solid the steel consists of a uniform solid solution containing 0.2 per cent. of carbon. A solid solution of carbon or carbide of iron in γ -iron is known as *austenite* and between the curves ad and ho the alloy under consideration consists of austenite having 0.2 per cent. of carbon in solid solution. The presence of carbon in solid solution in γ -iron lowers the temperature at which the change from γ to β iron takes place, as indicated by the curve

ho. When steel with 0.2 per cent. of carbon is cooled slowly the curve *ho* is reached at the temperature marked by the point 3. At this point β -iron begins to form and crystallises out of the austenite. As the β -iron holds no carbon in solution the austenite becomes progressively richer in carbon as the β -iron continues to separate. The temperature falls slowly while the β -iron is crystallising and the austenite becoming richer in carbon. At the temperature indicated by the point 4 (760°C.) the austenite has the concentration given by the point *o* (0.45 per cent. carbon), and the β iron which has separated changes into α -iron. α -iron now separates directly from the austenite, which then continues to become enriched in carbon, following the curve *of* until the temperature (690°C.) marked by the point 5 on the curve *gFK* is reached. The steel now consists of crystals of α -iron and residual crystals of austenite of the composition *f* (0.9 per cent. of carbon). Austenite with 0.9 per cent. of carbon is of the *eutectoid* composition and further loss of heat results in the simultaneous crystallisation at constant temperature of α -iron and carbide of iron *FeC*. α -iron is known as ferrite, carbide of iron is known as cementite, and the eutectoid mixture of the two is known as pearlite. Below the line *gFK* the steel consists of crystals of ferrite and crystals of pearlite, and no further change during cooling is marked on the diagram. The temperatures of the points 3, 4, and 5 are made evident during cooling by changes (retardations) in the rate of cooling and are known as the critical points. The highest of these points corresponding to the change of γ -iron to β -iron is known as Ar_3 , the middle one corresponding to the change of β -iron to α -iron is known as Ar_2 , and the lowest one due to the resolution of austenite into ferrite and cementite is known as Ar_1 . Ar_1 is also known as the *recalcescence point*, as in many cases undercooling takes place, and then when the transformation begins a rise of temperature, often considerable, is observed.

Considering next a medium carbon steel with about 0.6 per cent. of carbon, solidification takes place over the range of temperature between the points 6 and 7. Between the points 7 and 8 the steel consists entirely of austenite. At the point 8

on the curve of α -iron begins to separate direct from the austenite and Ar_3 is merged in Ar_2 . This point is commonly referred to as $Ar_{3, 2}$. On reaching the line gFK at the point 9 (the Ar_1 point) the residual austenite as before is transformed into pearlite. Ferrite and pearlite are thus the normal structure of this steel, but the proportion of pearlite is correspondingly greater than in a mild steel. In the case of a steel containing 0.9 per cent. of carbon no ferrite crystallises from the austenite, which remains unchanged until the temperature of the point 12 is reached when the whole breaks up into pearlite. The three critical points are now merged into one large recalescence point $Ar_{3, 2, 1}$.

With more than 0.9 per cent. of carbon, *e.g.* 1.4 per cent., solidification takes place over the range of temperature between the points 13 and 14. The steel then consists entirely of austenite until it has cooled to a point on the curve dF . At this point cementite begins to crystallise from the solid solution and the remaining austenite becomes poorer in carbon. Cementite continues to crystallise until the curve gFK is reached at the point 16 (Ar_1). The steel now consists of austenite of the composition F (0.9 per cent. carbon) and of some cementite. At this temperature the austenite changes into ferrite and cementite (pearlite) and the normal structure of such a high carbon steel is pearlite and cementite. At just over 2 per cent. of carbon (the point d on the diagram) the maximum amount of carbon that can exist in solid solution in γ -iron is reached, and this composition may be taken as the limiting composition for the alloys classed as steels; alloys containing more carbon are properly called cast irons.

A cast iron containing *e.g.* about 3 per cent. of carbon begins to solidify by the crystallisation of austenite at the temperature of the point 17. Austenite continues to crystallise until the temperature reaches that of the point 18 on the solidus curve dce , when the remaining liquid has the composition of the point C . This is the eutectic composition (4.3 per cent. of carbon), and the remaining liquid solidifies at constant temperature, forming an intimate mixture of crystals of austenite of composition d and cementite. On further cooling more cementite

separates, and the composition of the austenite follows the solubility curve df . At the temperature of the point 19 (690°C.) on the curve gFK the residual austenite is resolved into pearlite, and thus the white iron consists of large areas of pearlite representing the original primary austenite crystals separated by sheaths of cementite from a fine mixture of pearlite and cementite representing the eutectic of austenite and cementite. A white iron containing more than 4.3 per cent. of carbon deposits crystals of cementite during the first stage of solidification, until at the temperature of the point 21 the remaining liquid has the eutectic composition and a mixture of austenite, and cementite crystallises at constant temperature. Subsequently, as in the case of iron with less than 4.3 per cent. of carbon, a further quantity of cementite crystallises, and finally the residual austenite of the eutectic forms pearlite.

It will be evident from the above description that steels and white irons which have been cooled normally consist of ferrite and cementite, pearlite being merely a mixture of these two phases. The structural arrangement of these two phases, however, varies throughout the series, as is illustrated by the photo-micrographs, Figs. 22-29.

The specimens, from which the photo-micrographs were taken, were polished first on emery papers of increasing degrees of fineness and finally on a pad moistened with alumina. In order to develop the structure the specimens were etched in a 4 per cent. solution of picric acid in alcohol. After etching the ferrite remains white, and, when present in sufficient quantity and the etching prolonged sufficiently, the boundaries between each crystal grain are shown by fine black lines (cf. Figs. 22 and 23). The pearlite is distinguished by its brown or black colour at low magnifications, and at higher magnifications by the more or less clearly defined alternate light and dark striæ. The cementite remains unaffected by the etching agent and appears a brilliant white. It will be noted in the series of photo-micrographs that as the amount of carbon increases the quantity of pearlite increases, until with 0.9 per cent. of carbon, the steel consists entirely of pearlite. Further

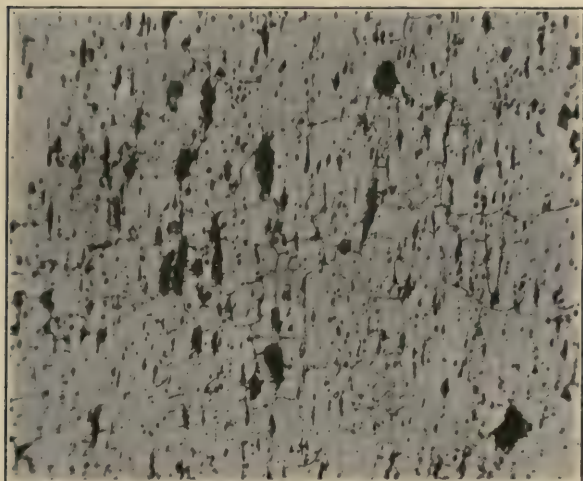


FIG. 22.—Wrought Iron of Good Quality. Longitudinal section. $\times 100$.
Consists only of crystals of ferrite with pieces of slag (black in photograph) which are elongated in the direction of rolling.

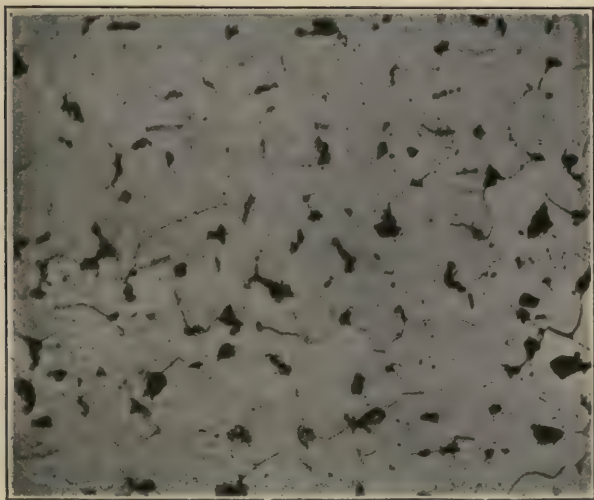


FIG. 23.—Mild Steel, 0.1 per cent. of Carbon. $\times 100$.
Consists of crystals of ferrite with a small quantity of pearlite (black).

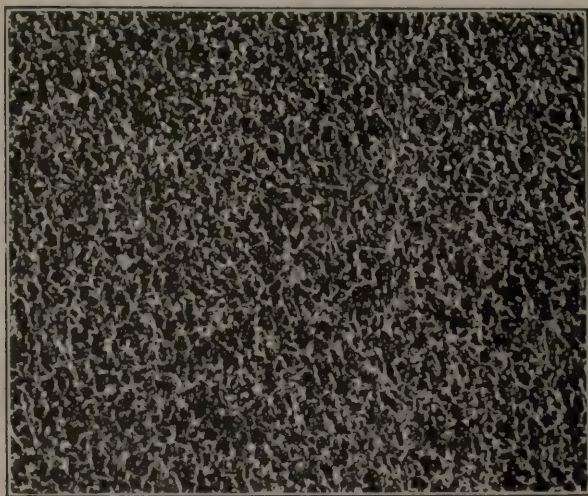


FIG. 24.—Steel, 0.41 per cent. of Carbon, as rolled. $\times 100$.
Ferrite (white), and pearlite (black).



FIG. 25.—Steel, 0.67 per cent. of Carbon, as rolled. $\times 100$.
Ferrite (white), and pearlite (dark).

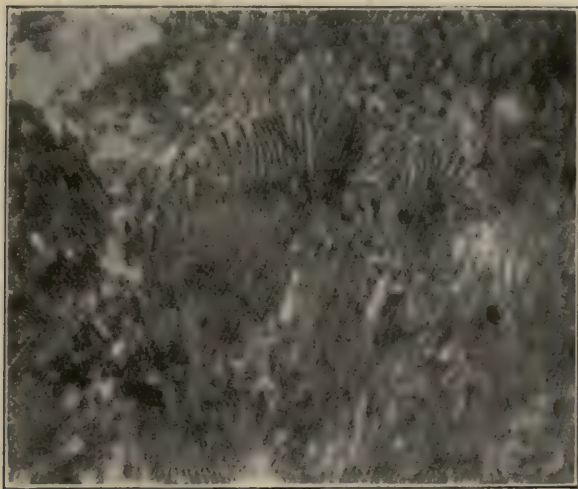


FIG. 26.—Steel, 0.9 per cent. of Carbon, annealed. $\times 1,500$.

Consists entirely of lamellar pearlite.

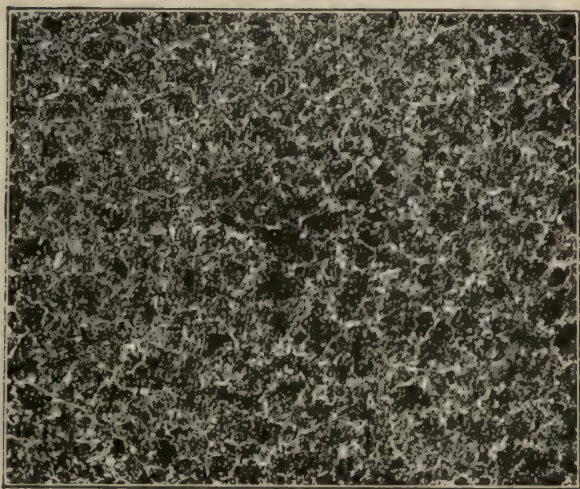


FIG. 27.—Steel, 1.4 per cent. of Carbon, as forged. $\times 100$.

Consists of pearlite (dark), and network of cementite (white).

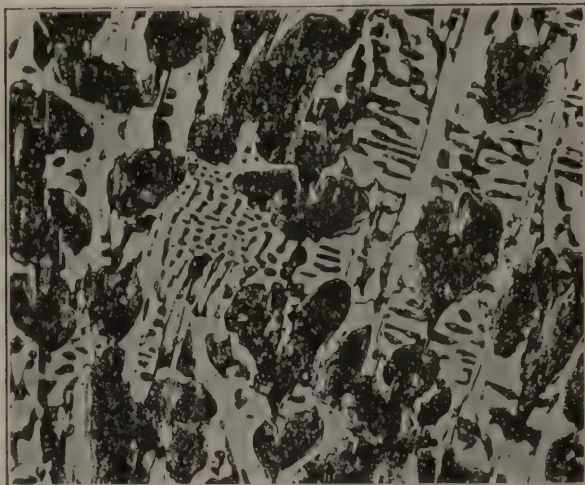


FIG. 28.—White Cast Iron, 3 per cent. of Carbon. $\times 100$.
Cementite (white), and pearlite (dark).

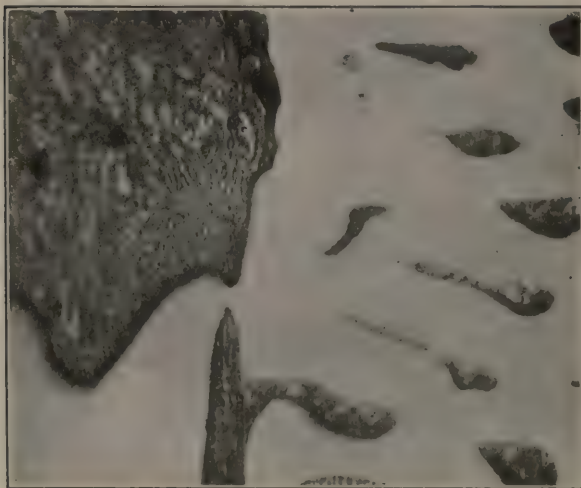


FIG. 29.—White Cast Iron, 3 per cent. of Carbon. $\times 1,000$.
Consists of cementite (white), and pearlite. The magnification is sufficient to show clearly the lamellar structure of the pearlite.

increases in the amount of carbon are then marked by increasing amounts of free cementite.

It has been explained on a previous page that the view is very generally held that cementite represents metastable equilibrium. The true stable phases in the solid alloys, according to this view, are austenite, ferrite, and graphite, austenite being stable at high temperatures, and ferrite at low temperatures. The stable diagram consists of the curves ac' , ad' , $c'b'$, $d'c'$, $c'e'$, and $d'f'$ of which ac' , ad' coincide with the curves of the metastable diagram, and the others are distinguished by being drawn as dotted lines. Completely stable equilibrium is practically never realised in the case of pure iron-carbon alloys, and consequently some of the curves of the stable diagram must be considered as more or less hypothetical. The diagram is, however, accepted as being at present the most reasonable way of recognising the presence of graphite in grey cast iron.

Iron-carbon alloys which solidify in a stable manner commence so doing by the crystallisation of austenite if their composition is to the left of the point c' , and by the crystallisation of graphite if their composition is to the right of the point c' . If the alloy contains more than the percentage d' (about 1.8 per cent.) of carbon the solidification is completed by the formation of the eutectic of graphite and austenite. Further cooling below the curve $d'c'e'$ results in crystallisation of graphite from the austenite (as indicated by curve $d'f'$), and finally below about 900°C . all the carbon exists as graphite, and the resulting γ -iron changes to β -iron and lastly to α -iron (ferrite).

The above summary of the stable equilibrium of the iron-carbon alloys is largely hypothetical, and in practice stable equilibrium is never entirely realised with pure alloys. Pure alloys containing less than about 4 per cent. of carbon under ordinary conditions always contain little or no graphite, and the influence of some impurity such as silicon is necessary to lead to the production of a grey iron. With more than about 4 per cent. of carbon there is no difficulty in obtaining a pure grey iron, although even here complete stable equilibrium could probably only be obtained by a very prolonged annealing.

In any case undercooling doubtless takes place, and the austenite-cementite eutectic forms instead of the austenite-graphite eutectic, the cementite subsequently decomposing to give graphite.

In commercial irons the influence of impurities, such as silicon, sulphur, and manganese, plays a very important part in determining whether stable or metastable equilibrium shall predominate, and all grades of iron from very grey to white are obtained with varying percentages of carbon.

The rate of cooling, as would be expected, also influences the character of the alloy to a marked degree, *e.g.* in the case of rapid cooling of steels when hardened by quenching in water. In this case the object of the quenching is to prevent to a greater or less degree the formation of pearlite from austenite. Rapid cooling also tends to produce white iron by preventing the formation of graphite, while slow cooling favours the formation of graphite and the production of grey irons. Annealing at suitable temperatures (900° to 1000° C.) also favours the decomposition of cementite and the separation of graphite in cast irons, and malleable castings may be obtained having very little carbon in the combined state.

The constitution of cast iron thus depends on the amount and kind of impurities present and on the rate of cooling and heat treatment, if any. Phosphorus gives rise to separate eutectics of comparatively low melting point (900° to 950° C.). The phosphide eutectic is thus a separate constituent of irons containing phosphorus. It varies considerably in appearance and composition in grey and white irons. Manganese sulphide is also present as a separate constituent in ordinary cast iron in the form of very small crystals throughout the iron. Some typical micro-structures of cast irons are illustrated in Figs. 30-39, white irons being illustrated by Figs. 28 and 29.

The photomicrographs show the variation in quantity and size of graphite in the different grades of iron. In a No. 1 iron or the softest of the series, the graphite is present in large quantity, and in the form principally of large, nearly flat plates. Such an iron contains the least amount of combined carbon in the series, and, consequently, the smallest quantity of

pearlite. In the irons higher in any series, the amount of combined carbon is greater and occurs entirely as pearlite or with free cementite in place of the ferrite of the softer and weaker irons (*e.g.*, No. 1 or No. 2), while the graphite is less in quantity and of a smaller and more irregular shape.

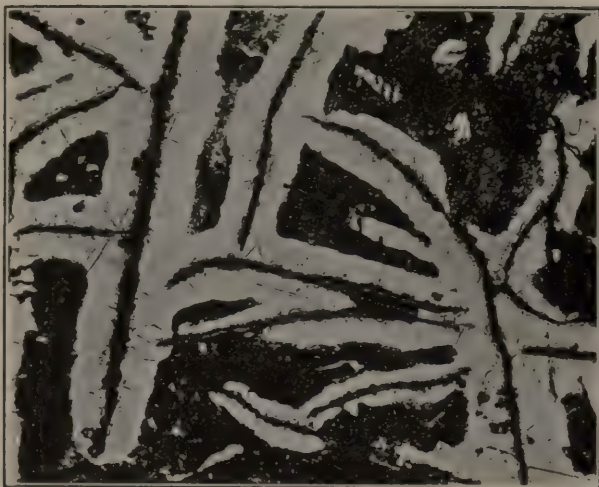


FIG. 30.—Hæmatite Grey Iron, No. 1 Bessemer. $\times 100$.

Consists of large, frequently straight, flakes of graphite (black), ferrite (white), and pearlite (dark or finely mottled). Note the arrangement of ferrite surrounding the graphite flakes.

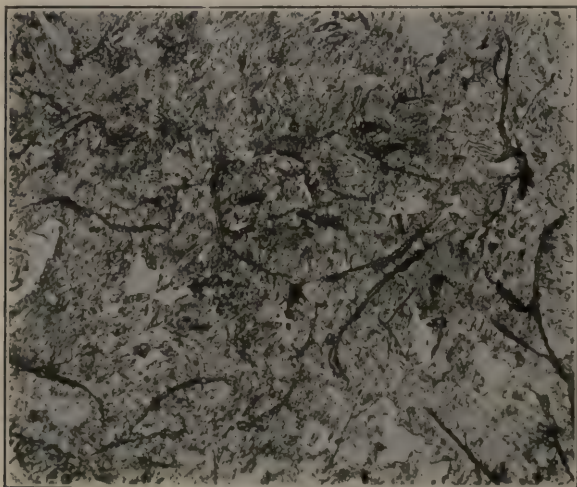


FIG. 31.—Hæmatite Grey Iron, No. 5 hard. $\times 100$.

Consists of flakes of graphite (dark), cementite (white), and pearlite (half-tone—black and white striae). Note small size and irregular shape of graphite, and that the cementite is free from graphite, which is always surrounded by pearlite unless free ferrite is present.

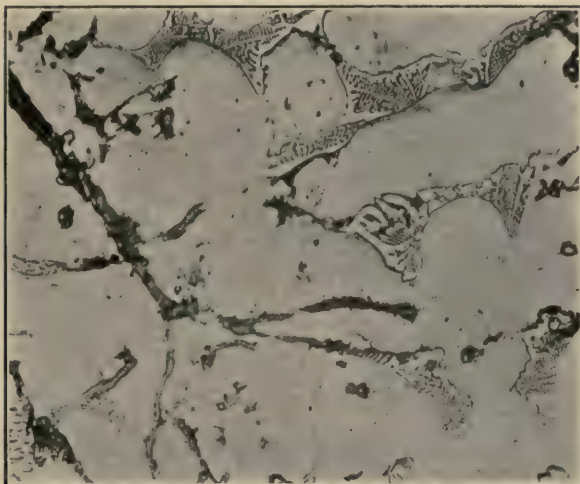


FIG. 32.—Soft silicious phosphoric Grey Iron, No. 1. $\times 100$.
Consists of graphite (dark), ferrite (white), and phosphide eutectic (mottled).
There is practically no pearlite present.

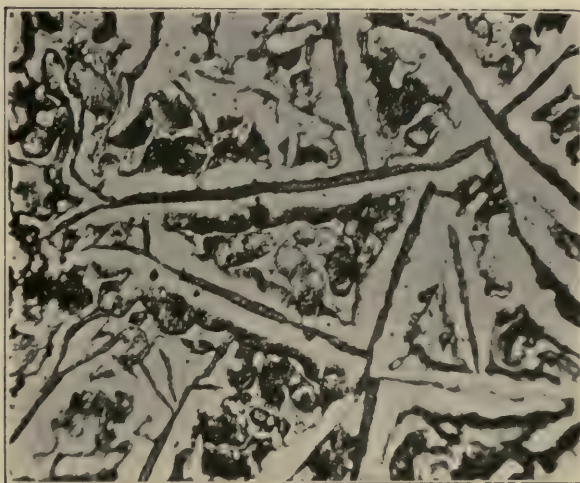


FIG. 33.—Soft phosphoric Grey Iron, No. 2. $\times 100$.
Consists of large graphite surrounded by ferrite (white). In the interior of the spaces bounded by graphite flakes are areas of phosphide eutectic (mottled), fringed with pearlite (dark).



FIG. 34.—Grey phosphoric Pig Iron. $\times 500$.
Shows phosphide eutectic, pearlite and graphite.

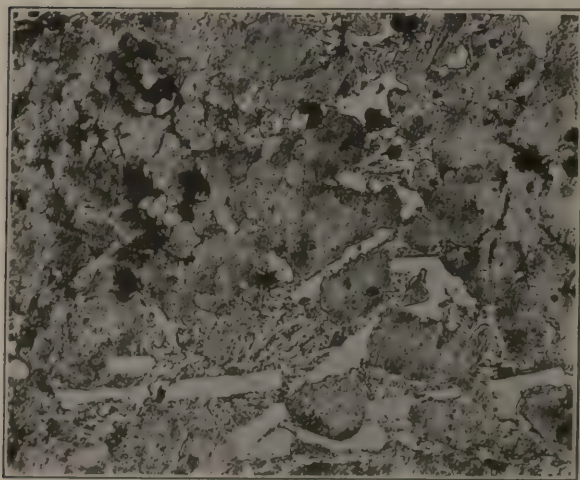


FIG. 35.—Hard phosphoric Grey Iron, No. 5 forge. $\times 100$.

Consists of small flakes and irregularly shaped particles of graphite (black), pearlite (finely striated), cementite (white), and phosphide eutectic (coarsely mottled). There is a large area of phosphide eutectic in the lower part of the photograph, surrounding a well developed crystal of cementite.

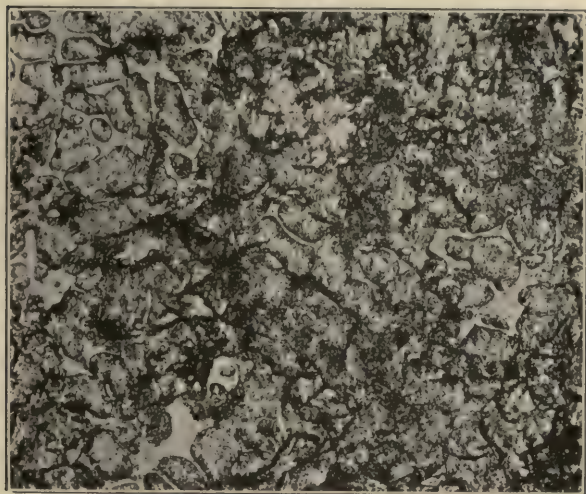


FIG. 36.—Strong Cylinder Iron. Tensile strength 17.9 tons per sq. in. $\times 100$. Shows small curved flakes of graphite (black) in a matrix of pearlite (half tone—striated). The light coloured constituent is phosphide eutectic.

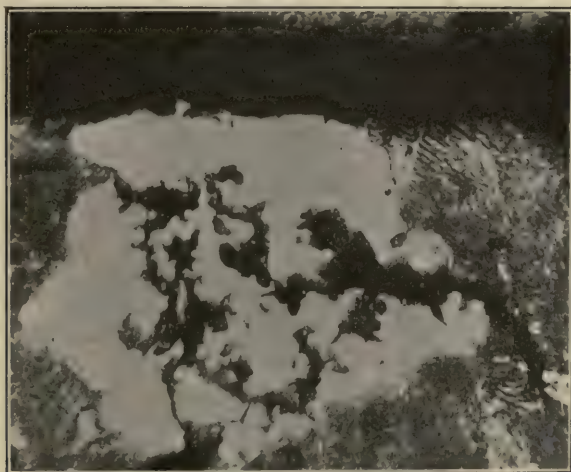


FIG. 37.—Grey Pig Iron. $\times 1,000$.

This photograph illustrates the variations in size and form of graphite in cast iron. The broad black border at the top is a portion of a large straight flake, and in the lower part are several irregularly shaped smaller pieces of different sizes surrounded by ferrite.

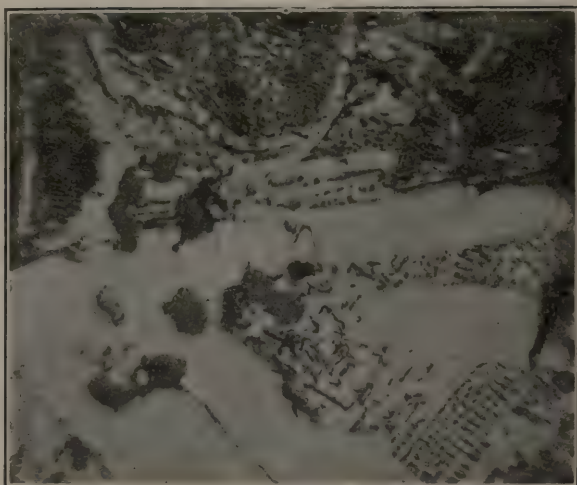


FIG. 38.—Hard phosphoric Grey Iron, No. 5 forge. $\times 1,000$.

Shows pearlite, phosphide eutectic, cementite and manganese sulphide, which is the clear dark grey constituent in the cementite and phosphide eutectic.

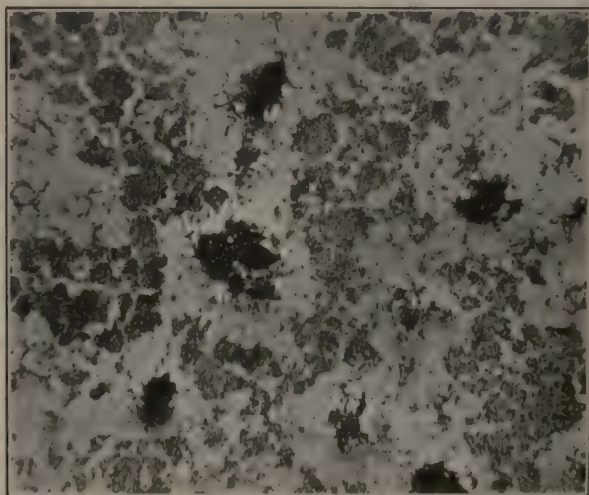


FIG. 39.—Malleable Cast Iron. $\times 100$.

Shows small black patches of temper graphite surrounded by ferrite (white).
The half tone areas are pearlite.

CHAPTER XIV

THE HEAT TREATMENT OF STEEL

HEAT treatment has for its object the control of the properties by suitable variations of thermal conditions. Heat treatment influences the properties of metals or alloys by modifying their constitution or by promoting changes in their crystalline character. The effect of heat treatment is closely connected with that of mechanical work.

Steel is always, except in special cases, forged or rolled while red hot and while the iron is in the γ -state holding the carbon in a state of solid solution. Steel at the rolling temperature has the constitution of a single-phase alloy, *i.e.*, it is essentially a uniform crystalline solution to which the name Austenite has been given. The effect of hot work on rolling or forging is to distort and break up the austenite crystals. At the working temperature, however, the austenite is capable of comparatively rapid crystalline growth after deformation, and if the rolling be stopped the austenite crystals rapidly grow from a number of new centres. During hot rolling the distortion of the crystals and their regrowth go on side by side. If we imagine that a piece of steel consists originally of, say, 100 large crystals of austenite, and if this piece of steel is worked, plastic deformation of the crystals takes place by slipping or gliding along a large number of cleavage planes, and at the same time many twinned crystals are also produced. Suppose now that the working is stopped, *e.g.*, in the interval between two "passes" of the rolls. Rapid crystalline growth then takes place, but instead of 100 distorted crystals growing again to normal shape, small portions of the crystals grow at the expense of others. If we suppose that crystal growth proceeds from 1,000 of these fractions, our piece of steel will in a very short time consist of 1,000 separate,

undeformed crystals. If the steel were to remain undisturbed at this temperature, certain of these crystals would continue to grow more rapidly than others and absorb them, and in time the piece of steel might again consist of only 100 crystals of austenite. If, on the other hand, as soon as the 1,000 new crystals had formed, rolling was started again, these 1,000 crystals would in their turn become deformed, and crystalline growth (on stopping the rolling) would start from, say, 5,000 new centres. Since this division of crystals and regrowth go on side by side during hot rolling, the longer the rolling is continued the smaller the crystals become; in other words, the greater the amount of work the finer the crystalline structure.

The rapidity and extent of the crystalline growth of the austenite varies with the temperature. At high temperatures it is so vigorous that the steel soon becomes dangerously coarsely crystalline and overheated, but at lower temperatures, not much above the critical points, the growth, after the crystals have attained a certain comparatively small size, is so slow that there is little further increase in size even after the lapse of a considerable time. Speaking generally, there appears to be a more or less definite austenite crystal size corresponding with each temperature, provided that the time of heating is not very widely varied. There are thus two chief factors governing the size of the austenite crystals when steel is forged or rolled hot, viz., the amount of forging or rolling, and the temperature at which that forging or rolling is finished. The finest structure is produced by hot working when the steel is thoroughly worked continuously from the reheating temperature down to the recalescence temperature. As soon as the critical temperatures are reached as indicated on the equilibrium diagram, ferrite (or cementite in the case of high carbon steel) begins to crystallise from the austenite, and when the A_{r1} point is reached all the residual austenite is transformed into pearlite. Although, however, the austenite crystals do not survive as such, their size determines the "grain-size" of the steel, *i.e.*, the size of the pearlite, ferrite and pearlite, or cementite and pearlite aggregates as the case may be. A fine grain-size is most desired in rolled steel, and this depends

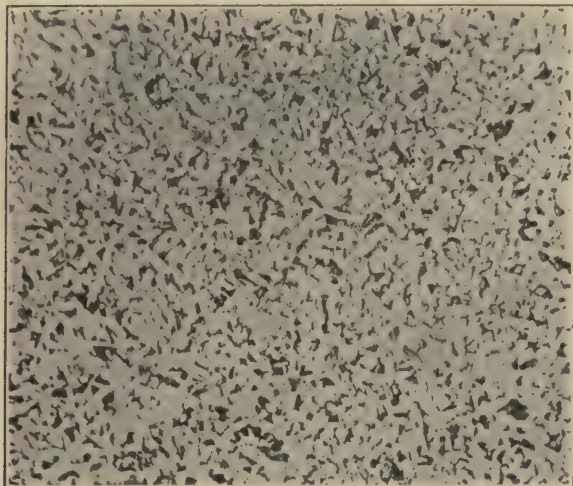


FIG. 40.—Steel, 0.25 per cent. of carbon, as rolled. $\times 100$.

Small grain size of well treated material.

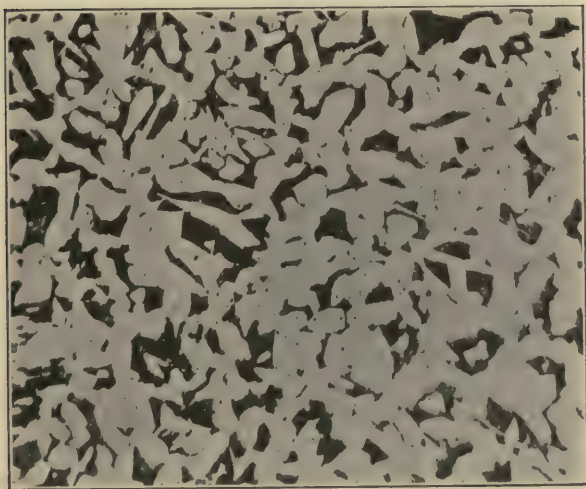


FIG. 41.—Steel, 0.25 per cent. of carbon, same steel as Fig. 40. $\times 100$.

Large grain size due to overheating.

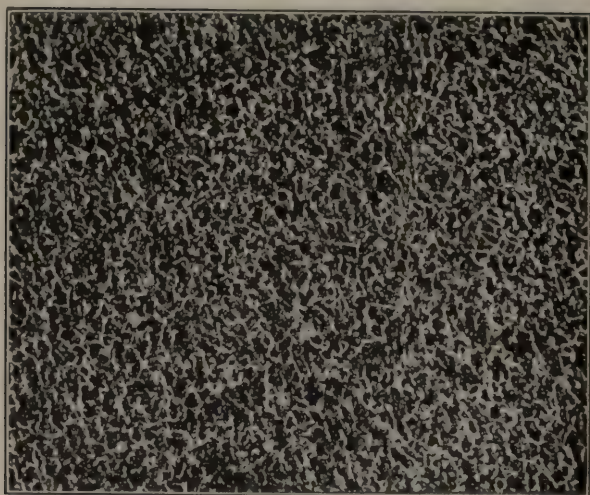


FIG. 42.—Steel, 0.41 per cent. of carbon, as rolled. $\times 100$.

Fine grained steel of good quality.

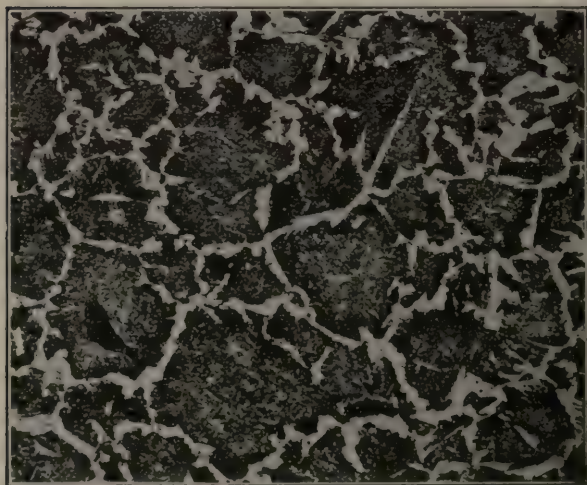


FIG. 43.—Steel, 0.41 per cent. of carbon, same steel as Fig. 42. $\times 100$.
Overheated. Note very coarse grain size and needle-shaped formation of ferrite

chiefly on the size of the austenite crystals when the rolling is finished, and the size of the austenite crystals depends on the reheating and finishing temperatures and on the amount of rolling. A large grain-size may result from one or more of the following causes: too high a reheating temperature, too small or ineffective amount of "work," or too high a finishing temperature. A dangerously large grain-size, as in overheated steel, is also accompanied by other structural characteristics, such as, in mild and medium carbon steel, spine-like projections of ferrite into the pearlite areas from a well-developed angular network of ferrite (see Figs. 40-43).

When steel is worked cold its hardness and "stiffness" is increased; its elastic limit and tensile strength are raised, while at the same time its ductility is reduced. These changes in mechanical properties accompany and are due to the permanent crystalline deformation produced by the cold working. The effect of cold work is not removed unless the steel is annealed, and in order completely to restore its softness and ductility the steel must be annealed at a temperature above the critical points, say 850°C. , and slowly cooled. Under these conditions the steel is brought back to the austenite condition and complete recrystallisation results. Steel cannot be cold-worked to an indefinite extent owing to increasing loss of ductility, and in many cases frequent annealings are required before the whole operation is finished. Usually it is necessary to carry out these annealings under conditions that will lead to the formation of little or no scale, and the work must be packed in closed boxes, or muffle furnaces are used in which a non-oxidising atmosphere can be maintained.

Steel that has been cold-worked may either—depending on the use to which it is to be put—be left in the cold-worked condition or may be given a final annealing.

Among examples of cold-working of steel are:

1. Wire and tube drawing. Usually several annealings are necessary, and wire or tube may be used in the hard-drawn or in the annealed condition. The hard-drawn material is used when great strength is required, *e.g.*, wire for wire ropes and piano wire.

2. Material required with a good surface finish, such as tinplates, while bars, *e.g.*, shafting, are sometimes finished by cold rolling, reeling, or drawing in order to obtain the exact diameter or section required together with a polished surface.

3. Steel strip is sometimes finished by cold rolling, as in the case of steel for pens and for lock fittings.

Annealing.—Steel is annealed in order to remove the effects of cold work, or of internal stresses resulting from work of any kind, and to remove the effects of rapid or irregular cooling. In the case of steel castings annealing is necessary on account of the great internal stresses due to shrinkage and in order to replace the original crystalline structure by a better and more uniform one. The annealing of cast, forged, or rolled material when properly carried out gives the maximum of ductility and an increase in the elastic limit, and the aim of annealing is to obtain the highest possible elastic limit which can be combined with the maximum ductility.

Usually the operation of annealing consists in uniformly heating the steel to a temperature between about 700°C. and 850°C. , although lower temperatures are sometimes employed, for a suitable time and cooling slowly. The correct temperature depends on the composition of the steel and the size of the article, while the time necessary depends principally on the size, as the whole piece should be uniformly heated to the same temperature throughout. Although not considered as such in the ordinary sense, the tempering of hardened steel and the reheating of ingots or billets are special cases of annealing.

Speaking generally, the best annealing temperature is just, but only just, above the critical points. The time of annealing should be such that the mass is heated to the same temperature throughout and the whole of the ferrite and cementite is transformed into a perfectly uniform solid solution—austenite. The treatment should result in uniformly small crystals of austenite, which on cooling give rise to steel having the best fine grain-size. Annealing at too high a temperature produces larger crystals of austenite and consequently a larger grain-size with inferior mechanical properties. Annealing at temperatures below the critical points may be sufficient to equalise any

internal stresses or remove the effect of too rapid or irregular cooling, but will not have the same refining effect as a suitable annealing at just above the critical points. Hardened steel that has been properly quenched from the correct temperature has already the best grain-size. Reheating or tempering at comparatively low temperatures up to about 650°C . gives a wide variation in mechanical properties by controlling the extent to which the change of martensite to pearlite takes place and by the release of internal stresses due to sudden cooling.

In the case of reheating for rolling or forging the temperature to which the steel is raised is usually much above that necessary to give the finest grain-size, but the subsequent working breaks up the large austenite crystals, as has been explained above. Steel is thus produced having a more or less fine grain-size depending on the extent and character of the rolling or forging. Such a refining of structure may be distinguished as "mechanical refining." For many purposes the steel is still further improved by a subsequent "heat refining" or annealing.

Hardening.—When steel is suddenly cooled from a temperature above the critical points it is hardened. The degree of hardness obtained depends chiefly on the amount of carbon present. A mild steel can be hardened only to a small extent, but the hardening power increases with the percentage of carbon up to nearly 1 per cent. The amount of hardening also depends on the rapidity of cooling, and also to some extent on the temperature from which the steel is quenched.

When steel is in equilibrium at temperatures above the critical points it consists of a uniform solid solution of carbon in γ -iron, and this solid solution is known as austenite. Under normal conditions at ordinary temperatures steel is composed of a mixture of α -iron (ferrite) and carbide of iron (cementite) either entirely in the form of pearlite or with ferrite or cementite in excess. The change of austenite to ferrite + pearlite, pearlite, or pearlite + cementite is with slow cooling completed at the A_{r1} point or 690°C ., and the steel at the ordinary temperature is soft. When quickly cooled, however, the change is more or less completely suppressed and the steel is hardened. In the case of ordinary carbon steels the austenite is never

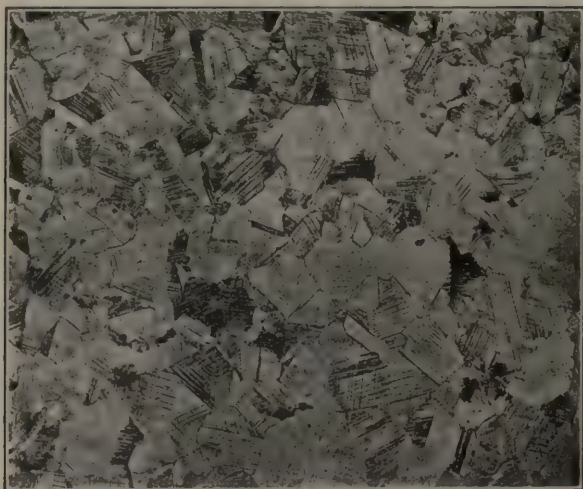


FIG. 44.—Special Manganese Steel (11 per cent. manganese), rolled. $\times 100$
Consists of austenite.

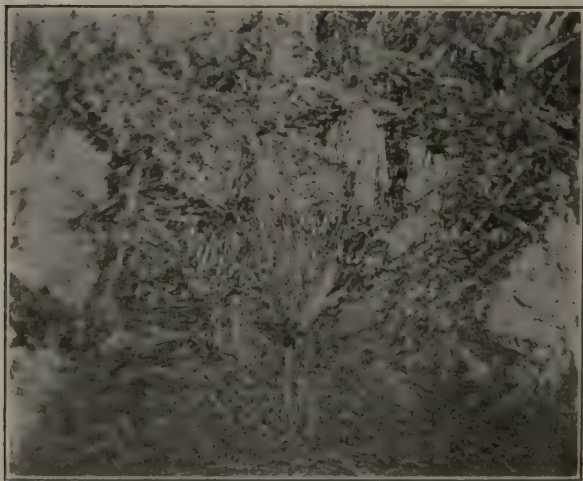


FIG. 45.—Steel, containing 0.45 per cent. of carbon, hardened. $\times 100$.
Consists of martensite.

completely retained as such at the ordinary temperatures, even under the most vigorous quenching conditions. Austenite (Fig. 44), as seen in some special steels, such as nickel steel and manganese steel, has the normal polygonal structure of solid solutions, but in carbon steels quenched under ordinary conditions the structure found is a characteristic acicular one known as martensite * (Fig. 45). Martensite probably does not represent austenite in a completely metastable condition, but is usually considered to be the first stage of its resolution into ferrite and cementite. Other stages are recognised, and have been given separate names, as each when suitably etched has a distinct appearance under the microscope. The usual stages recognised are :

Austenite—martensite—troostite—sorbite—pearlite.

Troostite, which etches and darkens uniformly and readily, is probably an exceedingly fine, ultra-microscopic mixture of ferrite and cementite.

Sorbite appears to be a very finely granular form of pearlite.

Martensite is exceedingly hard and, except when containing only small amounts of carbon, will scratch glass. It is, however, very brittle, and hardened steels consisting entirely of martensite are of little use.

Tempering.—In order to reduce the extreme brittleness of martensite the hardened steel is tempered or reheated at low temperatures. The operation of tempering usually consists in heating the steel to some definite temperature (between about 200° C. and 650° C.) and then cooling either quickly or slowly. In tempering tool steels for different purposes the necessary temperature is in practice commonly judged by the colour of the oxide film formed on the surface, this colour varying with the temperature from a light straw to deep blue. The change of austenite to ferrite and cementite is still further completed by tempering, and according to the heat treatment the martensite passes partly or wholly into troostite and then into sorbite

* Martensite appears to be composed of innumerable fine lines or needles intersecting each other at angles of 60°. These lines represent octahedral cleavage planes of the austenite and are probably due to the very high internal stresses set up by the sudden cooling.

with higher temperatures, the hardness and brittleness decreasing accordingly and the ductility increasing.

The proper temperature for quenching varies with the composition of the steel. It should be only just above the critical points, as otherwise the increased crystal size of the austenite gives rise to a coarse-grained material of inferior properties. For ordinary carbon steels the quenching temperature varies from about 700°C. to a little over 800°C. , and for any particular steel is confined within the narrow limits of a few degrees if the best results are to be obtained. The degree of hardness obtained depends on the rapidity with which the steel is cooled through the critical range, and this in turn depends partly on the quenching temperature and partly on the quenching medium and also to some extent on the size of the piece of steel. The quenching liquid usually used is water, and ice cold water gives greater hardness than warm water. Oil and melted lead are also used as quenching liquids, and these give a tougher and less brittle although less hard material. Mercury and iced brine may be used to give extreme hardness. Water and even oil quenching gives a material that is too brittle and unnecessarily hard for many purposes, and the hardening effect must be modified by a subsequent further heat treatment, *i.e.* tempering.

CHAPTER XV

SPECIAL STEELS

WITHIN recent years a most important development in the metallurgy of steel has been the use of other metals to improve its properties in certain respects and to increase its range of usefulness. Such steels, in which one or more other metals such as nickel, manganese, chromium, vanadium, and tungsten, besides iron, are essential components of the alloys, are known as special steels or alloy steels. The metals used to produce special steels are all more or less soluble in α -iron at the ordinary temperatures and in γ -iron at high temperatures, some of them, like nickel and manganese, forming with iron unbroken series of solid solutions from 0 to 100 per cent. of iron. Many of these alloy metals also form carbides which are isomorphous with carbide of iron and separate with it either as a definite double carbide or held in solid solution. At first the alloy metal has little effect on the constitution of the steel, which when normally cooled has the usual pearlite or ferrite and pearlite structure. In many cases increasing quantity of the added metal sooner or later (depending on the metal added and the amount of carbon in the steel) causes the steel to exist in the martensitic state when cooled slowly to the ordinary temperature, and still further addition eventually gives a steel whose normal constitution is austenite, the structure being the usual polygonal one common to all solid solutions. In other cases the austenitic or both martensitic and austenitic stages are not reached, but instead a double carbide makes its appearance. Usually the special steels that are of industrial value have either a pearlitic or austenitic structure, and those that are martensitic or contain a free double carbide are useless. Although alloy steels may be thus classified in a general way and certain common characteristics can be recognised, the effect of each metal must

be considered separately, as each impresses on steel more or less markedly a distinct individuality.

Nickel Steel.—Nickel and iron are mutually soluble in each other in all proportions in both the liquid and the solid state, and in nickel steels the nickel exists always in a state of solid solution. The nickel steels that are most largely used contain 3 or 4 per cent. of nickel or less and low percentages of carbon, and are in fact mild steels carrying a small quantity of nickel. On adding successive amounts of nickel to a steel the elastic limit and tensile strength are both at first much improved and rise to a maximum, after which further additions of nickel cause a decrease of strength. The elongation decreases only slowly at first until the strength of the steels approaches its maximum. The ductility then rapidly diminishes with further increase in the percentage of nickel, and the steels become quite brittle, and remain so over a more or less extended range of composition. With still larger percentages of nickel ductility is regained. The influence of nickel on the properties of steel is more marked in the case of high carbon steel than in the case of mild steel, the brittle range in steels with 1 per cent. of carbon extending from 4 to 12 per cent. of nickel, and with 0·2 per cent. of carbon from about 8 to 20 per cent. of nickel. The following table* shows the effect of varying percentages of nickel on steels of medium carbon.

Composition.			Yield Point, tons per sq. in.	Maximum Stress, tons per sq. in.	Elonga- tion, per cent. on 2 in.	Contraction of Area, per cent.	Bending Test, Bent to— U Unbroken B Broken.
Ni, per cent.	C, per cent.	Mn, per cent.					
—	0·47	0·95	21·00	38·19	25·0	51·73	180° U
1·20	0·48	0·75	23·93	40·93	21·0	42·80	180° U
2·15	0·47	0·86	23·67	41·52	24·5	51·83	180° U
4·25	0·40	0·82	29·16	47·86	20·0	33·06	180° U
4·95	0·42	1·03	33·95	60·09	2·0	3·71	30° B
6·42	0·52	0·92	None detected	110·57	Nil.	Nil.	10° B
7·95	0·43	0·79	None detected	77·38	Nil.	Nil.	5° B
12·22	0·41	0·85	34·56	80·24	1·0	1·63	10° B
15·98	0·45	0·83	28·53	80·24	5·5	7·33	60° B
19·91	0·41	0·96	15·33	43·92	55·0	63·11	180° U

* Figures taken from the 7th Report of Alloys Research Committee, *Proc. Inst. Mech. Eng.*, 1905, p. 878.

Constitution and Structure of Nickel Steels.—The strong, ductile, and useful nickel steels with comparatively small percentages of nickel have the normal pearlitic structure, and the ductile alloys with high percentages of nickel, and also useful for certain purposes, show a simple austenitic structure. Very low carbon nickel steels consist of ferrite and pearlite with nickel up to nearly 10 per cent. and do not become austenitic until the amount of nickel present approaches 30 per cent. The effect of nickel becomes more and more marked as the carbon increases. Thus with 0·8 per cent. of carbon the pearlitic range extends only up to about 5 per cent. of nickel, and austenitic steels are reached below 15 per cent. of nickel. Intermediate between the pearlitic and austenitic steels are the hard, brittle, and useless alloys which consist of martensite under ordinary conditions. The martensitic steels are, however, not sharply separated from the pearlitic steels on the one hand or the austenitic steels on the other, but transition structures may be recognised over small ranges of percentage of nickel.

The constitution of the nickel steels as outlined is connected with the influence that nickel exerts on the transformations (Ar_3 , Ar_2 , and Ar_1) of ordinary carbon steels. It was shown by Osmond in studying the effect of nickel on low carbon steels that the transformation temperatures are lowered. With 4 per cent. of nickel Ar_3 and Ar_2 are united at about 640° C., and with 8 per cent. of nickel Ar_3 , Ar_2 , and Ar_1 are united to give one transformation at 510° C. This lowering of the transformation temperatures is greater with higher percentages of nickel and is more marked in higher carbon steels. It will thus be seen that as the nickel increases the transformations are more and more easily suppressed on cooling, and in the case of the martensitic steels they have not taken place under normal cooling conditions, while in the austenitic steels the transformation temperatures are not much above the ordinary temperature or are even below it.

Iron in the γ state (austenite) is non-magnetic, and the austenitic nickel steels are consequently not magnetic. Hopkinson has shown that a 25 per cent. nickel steel is non-magnetic at the ordinary temperature, but that when cooled to

0° C. it becomes slightly magnetic, while at -50° C. it is strongly magnetic. On raising the temperature the steel remains magnetic until a temperature of 580° C. is reached, the magnetic change not being a reversible one.

The effect of nickel on the dilatation of iron is of considerable importance. On adding nickel the dilatation decreases up to 36 per cent. of nickel * when the alloys undergo practically no alteration in volume with rise of temperature or even in some cases contract slightly. On increasing the nickel beyond 36 per

MECHANICAL PROPERTIES OF MANGANESE STEELS.

Composition.			A		B	
Mn., per cent.	C., per cent.	Si., per cent.	Max. Stress, tons per sq. in.	Elongation, per cent. on 8 ins.	Max. Stress, tons per sq. in.	Elongation, per cent. on 8 ins.
0.83	0.20	0.03	33	31		
2.30	0.40	0.15	56	6		
3.89	0.40	0.09	38	1		
7.22	0.47	0.44	27	2	25	2
10.6	0.85	0.28	34	4	40	17
12.81	0.92	0.42	39	5	61	37
13.75	0.85	0.23	—	—	64	50
14.48	1.10	0.32	39	1	63	37
19.10	1.60	0.26	52	1	59	4

A. Tested as forged. B. Reheated to yellow heat and cooled in water (water toughened).

cent. the dilatation increases again rapidly. It is thus possible to select alloys of almost any desired coefficient of linear expansion between zero and that of nickel from among the high nickel or austenitic nickel steels. These alloys are ductile and fairly strong and resist corrosion very much better than ordinary steel. Alloys of this type may be obtained which are non-magnetic. An alloy known as "Invar" containing 36 per cent. of nickel and 0.2 per cent. of carbon is practically non-expandable and is used for standards of length and for measuring tapes, etc. Another alloy called "Platinite," which contains 46 per cent. of nickel and 0.15 per cent. of carbon, has the

* Guillaume, *Bull. de la Société d'Encouragement*, 1898, and *Comptes Rendus*, Vol. CXXXVI.

same coefficient of expansion as glass and is used in the construction of incandescent electric lamps.

Manganese Steels.—Manganese is always present in ordinary commercial steels in varying amounts from about 0·3 to 1 per cent. Beyond about 1 per cent. manganese begins seriously to affect the ductility of steel, and with less than 5 per cent., the amount depending on the percentage of carbon present, the steels are quite brittle. The alloys remain very brittle and hard over a range of percentage of manganese, but further increase is accompanied by a return of ductility and decrease of hardness.

The table on page 132* shows the variation in mechanical properties with different percentages of manganese and carbon.

Constitution of Manganese Steels.—In constitution and structure the manganese steels resemble in a general way the nickel steels. Manganese, like nickel, lowers the transformation temperature, but the effect of manganese is more pronounced, 10 per cent. of manganese in mild steels lowering $A_{r_3, 2, \text{ and } 1}$ to below the ordinary temperatures. The influence of manganese, as in the case of nickel, is more marked the higher the carbon. With low carbon the steels are pearlitic to about 4 per cent. of manganese, and with higher carbon, say 1 per cent., the steels are pearlitic only below 3 per cent. Mild steels from about 5 to 10 per cent. are martensitic and with higher percentages are austenitic. There are also small ranges of percentages of manganese in which the steels have transition structures between pearlitic and martensitic, and martensitic and austenitic. In the higher carbon steels those in the brittle, hard range are not very characteristically martensitic, but, according to Guillet, have a structure resembling troostite. Manganese forms a double carbide with iron, and the pearlite of low manganese steels is less lamellar in character than ordinary pearlite, but is more broken up and granular. The higher manganese steels, following the lowering of the transformation temperatures, are non-magnetic, but, unlike nickel, manganese does not give rise to non-expansible alloys.

* Hadfield, *Proc. Inst. Civil Eng.*, Vol. XCIII., 1888, Part III., p. 1.

Commercial Manganese Steels.—It follows from consideration of the constitution of the manganese-iron-carbon alloys that it is only the austenitic steels that are useful. The pearlitic steels resembling the nickel steels are too deficient in ductility to be of value, unless the ordinary carbon steels with less than 1 per cent. of manganese be taken to represent this class. Our knowledge of the properties of manganese steels is largely due to the work of Hadfield, who is also responsible for their introduction as commercial steels. The well-known Hadfield's manganese steel contains about 13 per cent. of manganese and 1 per cent. of carbon. It is very strong, tough, and hard, and is used in the cast condition. It is somewhat softened by quenching from a yellow heat and is hardened again by reheating and allowing to cool slowly, but in any case is exceedingly difficult, if not impossible, to machine. Manganese steel is used for such purposes as tramway points, parts of crushing machinery, and other purposes where great strength combined with hardness and resistance to wear are demanded.

Chromium Steels.—Chromium in small quantities slightly raises the tensile strength of steel and does not seriously affect its ductility. In larger quantities chromium causes brittleness, and, unlike nickel and manganese, still larger additions are not accompanied by a return of the ductility. The effect of chromium depends on the amount of carbon present; the higher the carbon, the more marked is the effect of chromium. Chromium, although not possessing by itself the property of causing iron to harden on quenching, increases the hardness and hardening power of carbon steels.

Constitution of Chromium Steels.—With low percentages of carbon the steels remain pearlitic until the amount of chromium is between 5 and 7 per cent. Between 7 and 15 per cent. of chromium the steels are martensitic under ordinary conditions of cooling, but a still larger amount of chromium does not yield a less hard and brittle steel consisting of austenite only, a double carbide of chromium and iron separating as small white and hard particles. Unlike manganese and nickel, chromium does not lower the critical points

in steel, but raises the A_1 points, leaving the A_2 points unaffected. It has been shown recently that with 6 per cent. of chromium the Ac_1 point is actually raised above the Ac_2 point.*

Vanadium Steels.—Small quantities of vanadium exert a very powerful influence on the properties of steel, small quantities having a very marked influence on the mechanical properties. Vanadium forms a double carbide with carbon and iron, which separates as a separate constituent of the steel when the amount of vanadium present exceeds about 0·7 per cent. When the vanadium is present in amounts which are less than that required to lead to the separation of the double carbide the slowly cooled steels have the ordinary pearlite structure. Until the appearance of the double carbide the elastic limit, maximum stress, and hardness increase rapidly with increase of vanadium, while the elongation is not seriously affected and the steels do not become brittle. The separation of the double carbide which follows further increase of vanadium is accompanied by brittleness and a reduction of strength. The pearlitic vanadium steels consequently are the only ones of value, and less than 0·5 per cent. of this metal is present in vanadium steels. Vanadium increases the hardening power of carbon steels, but vanadium steels are not self-hardening. The pearlitic steels are hardened by quenching in the same way as ordinary steels.

Vanadium is usually used in alloy steels in conjunction with another metal to form quaternary alloys of which the chrome vanadium steels are the most important.

Titanium Steels.—Titanium occurs widely and fairly abundantly in nature, and, although not easily reduced in the blast furnace under ordinary conditions, is present sometimes in small quantities in pig iron. Ferro-titanium with various proportions of titanium is made in the electric furnace at comparatively low cost, and within recent years has found considerable use as an addition to steel and cast iron. Titanium is said to increase the strength of steel, but its direct influence on the mechanical properties probably is not very great. Indirectly, however, it has a very marked effect, since it combines readily with

* Moore, *Jour. I. and S. Inst.*, 1910, Vol. I., p. 268.

oxygen, and has also a strong affinity for nitrogen. When used in steel-making, the titanium (in the form of ferro-titanium) is added in the ladle, replacing the aluminium and part of the usual ferrosilicon addition. Generally little, if any, titanium remains in the steel, but its effect is marked by greater soundness and improved strength, toughness, and wearing qualities. The advantage of titanium as an addition to steel is considered to be due in a large measure to its power of removing nitrogen. The effect of nitrogen on the mechanical properties of steel is not known accurately, and even the amount commonly present is a matter of uncertainty. It is, however, probable that it has a distinctly injurious effect, resembling that of phosphorus on the mechanical properties. Titanium steel (or "titanium treated") steel is used for rails, which are stated to give exceptionally good results in practice.

Titanium appears to have little direct effect on the structure or constitution of steels. Although titanium lowers the A_{r_3} point, it has little influence on either A_{r_2} or A_{r_1} , and steels with as much as 10 per cent. of titanium have the normal pearlitic structure.

The use of titanium in small quantities in manganese steels promises to give results of great value. Manganese titanium steel with 11 per cent. of manganese, 1 per cent. of carbon, and a small quantity of titanium—up to 0.4 per cent.—is readily forged and rolled and can be machined easily. It is extremely hard, yet very strong and tough, having a tensile strength of 65 to 70 tons per square inch, and an elongation of 45 per cent. on a 2-inch length.

Tungsten Steels.—Tungsten in the absence of carbon has no very marked effect on the mechanical properties of iron, but in carbon steels it greatly increases the hardness and hardening power. It is stated that some of the steels of the highest reputation in past times, such as the sword blades of Damascus, owed their excellence to the presence of small quantities of tungsten. The first notable instance, however, of the intentional use of tungsten to modify the properties of ordinary steel was the introduction by Mushet some 45 years ago of his "Special Steel" which contains 5 to 8 per cent. of tungsten

and 1.5 to 2.3 per cent. of carbon. Mushet's steel is self-hardening—that is to say, by heating to a red heat and allowing to cool in air it is hardened.

The constitution of tungsten steels depends on the amount of carbon present as well as the tungsten. When the amount of carbon is small the steels are pearlitic until the tungsten reaches about 10 per cent. Beyond this limit an increase of tungsten causes the separation of a double carbide of iron and tungsten, and there is no intermediate martensitic stage. In the presence of a larger proportion of carbon the effect of tungsten is more marked, and in high carbon steels the double carbide makes its appearance when the tungsten exceeds about 5 per cent. Tungsten increases the tensile strength and hardness of steel without much increasing the brittleness unless the tungsten is present in sufficient quantity to cause the separation of the double carbide. The presence of the double carbide in increasing amounts is followed by a rapid increase in both hardness and brittleness, and although the tensile strength is great the elastic limit and elongation decrease.

Besides its use in self-hardening steels and in high speed tool steels, tungsten steels, containing about 0.5 per cent. of carbon and less than 1 per cent. of tungsten, are used for springs, and steels with 4 to 8 per cent. of tungsten according to the amount of carbon present are used for permanent magnets.

Molybdenum Steels.—The effect of molybdenum in steel closely resembles that of tungsten, but is much more marked. One per cent. of molybdenum has an equivalent effect of about $4\frac{1}{2}$ per cent. of tungsten. Molybdenum to the extent of 3 to 4 per cent. with 1 to 1.5 per cent. of carbon is used in steels for permanent magnets, molybdenum, it is stated, being better than tungsten for this purpose. Molybdenum is also used in some tool steels, usually replacing part of the tungsten.

Special Tool Steels—Self-Hardening Steels.—Ordinary carbon steels are hardened by heating them to a red heat and then cooling them very suddenly by quenching in water. Excessive brittleness is removed and the right degree of hardness obtained by a subsequent reheating at a low temperature between about 200° C. and 350° C. If ordinary steels are slowly cooled from

a red heat they remain unhardened and are useless as tools, while the range of temperature from which quenching gives satisfactory results is a comparatively limited one of about 20 or 30 degrees.

Mushet in 1868 discovered that steel containing tungsten was hardened by ordinary cooling and that it was not necessary to quench such steel. The quenched steel, in fact, was not so hard as the slowly cooled steel. This discovery led to the introduction of Mushet's "Special Steel," followed by many others of a similar character, all known generally as "self-hardening steels." After Mushet's steel had been introduced it was shown by Gladwin and others that the cutting properties of the steel could be improved by cooling in an air blast after reheating. Self-hardening steels are also known as air-hardening steels, and this soon became the usual method of hardening. The following is given as the composition of Mushet's original self-hardening steel :—

Carbon	2·0 per cent.
Tungsten	5·0 ,,
Chromium	0·5 ,,
Manganese	2·5 ,,
Silicon	1·3 ,,

and generally all the self-hardening steels contain from 5 to 10 per cent. of tungsten together with small amounts of chromium or manganese, or both. Occasionally part of the tungsten is replaced by molybdenum, and in all cases the presence of small percentages of manganese or chromium appears to be essential.

The self-hardening steels are much superior in cutting power to ordinary tool steels. They can be used at higher speed (two or three times as great) and are capable of cutting harder metal than carbon steels. It was not, however, until the development of high speed steels many years after the introduction of Mushet steel that cutting speeds were increased generally to any great extent, the self-hardening steels being considered of value on account of their much superior resistance to wear under normal conditions or when cutting at slightly increased speeds. Also the power of cutting satisfactorily metal that formerly it was

impossible or too costly to machine added greatly to the usefulness of self-hardening steels.

High Speed Tool Steels.—For many years self-hardening steels were generally treated by reheating to a temperature such as would be suitable for a carbon steel, although Mushet had originally recommended that his special steel should be heated to a scaling or yellow heat before cooling. It was not until the work of Taylor and White at the Bethlehem Works in 1898 demonstrated its value that the importance of high heat treatment was recognised. Taylor and White in experiments on the cutting speeds of tool steels were able to show conclusively that heating to a yellow heat before cooling enormously improved the cutting speed of self-hardening steels. The properties and cutting speed of a self-hardening steel are deteriorated by heating to the neighbourhood of about 875°C . This deterioration increases until a temperature of reheating of 925°C . is reached, after which high temperatures cause a rapid increase in cutting speed and improvement in properties. The cutting speed of a tungsten self-hardening steel that is reheated to 1050°C . or 1100°C . is three or four times that of the same steel reheated to 825° to 850°C . As soon as the importance of the heat treatment at a high temperature became generally known high speed steels were rapidly developed from the older self-hardening steels, and enormous improvements in machine shop practice followed. It may, however, be noted that many high speed steels do not differ greatly in composition from self-hardening steels, the improvement being mainly a question of heat treatment. The differences in composition of self-hardening and high speed steels are mainly those of degree, the amounts of alloy metals, tungsten, molybdenum, and chromium principally, being greater in the high speed steels. The important difference in properties lies in the fact that high-speed steels retain their hardness even after heating up to a dull red heat, *i.e.*, they have the properties of red-hardness. Red-hardness is conferred on the steel by the high heat treatment, and a steel may be self-hardening but yet have no red-hardness. The general quality of high speed steels has been greatly improved since their introduction. At first a fine

cutting edge was not obtained and they could be used only for roughing work, but now they can be given an edge suitable for the finest finishing work, and they are even used with advantage in wood turning. The following table gives the composition of some high speed tool steels :—

—	1	2	3	4	5	6	7	8
Carbon	0·674	0·54	0·9	0·67	0·76	0·93	0·87	0·60
Tungsten	18·19	10·08	22·8	20·7	18·85	24·5	18·77	30·20
Molybdenum . . .	—	4·38	—	—	—	—	—	—
Chromium	5·47	3·0	8·1	3·7	2·95	7·19	1·22	3·70
Manganese	0·11	0·16	0·47	0·14	0·42	0·23	0·27	0·24
Vanadium	0·29	—	—	—	—	—	—	—
Silicon	0·43	—	0·20	0·15	0·33	0·24	0·11	0·23

1. Becker, "High-Speed Steel," p. 48.

2. *Ibid.*, Appendix, Analysis No. 44.

3. Eight Steels from different makers, foreign and English, *Iron and Coal Trades Review*, Vol. LXXXII., p. 876; also *Journ. Iron and Steel Inst.*, 1911, Vol. II., p. 623.

The following composition has been recommended by Taylor* for the best high speed tool steel :—

Carbon	0·682 — 0·674 per cent.
Tungsten	17·81 — 18·19 „
Chromium	5·95 — 5·45 „
Manganese	0·07 — 0·11 „
Vanadium	0·32 — 0·29 „
Silicon	0·49 — 0·43 „

and a recent specification† of the U.S. Navy Department for high speed steels is :—

Carbon	0·75 — 0·55 per cent.
Tungsten	20·0 — 16·0 „
Chromium	5·0 — 2·50 „
Manganese	0·30 — 0·5 „
Vanadium	0·00 — 0·35 „
Silicon	0·30 — 0·00 „
Sulphur	0·02 — 0·00 „

* F. W. Taylor, *Am. Machinist*, Vol. XXIX., pp. 763—766; also *Journ. I. and S. Inst.*, 1907, Vol. I., p. 537.

† *Iron Age*, Vol. LXXXVII., pp. 1568—1569; also *Journ. I. and S. Inst.*, 1911, Vol. II., p. 623.

CHAPTER XVI

STEEL CASTINGS

THE production of steel castings is now an important branch of steel manufacture. They are used in a number of cases where formerly forgings were employed and in other cases where it is required to have greater strength and toughness than is possessed by cast iron. Among examples of steel castings are stern frames, shaft brackets, railway wheels, gear wheels, and crank axles.

Steel used for Castings.—This may be manufactured by either the crucible, Bessemer, or open hearth processes, and is generally mild or medium carbon steel. High carbon steel is rarely suitable and is not often used. In the majority of cases the steel used contains about 0·3 per cent. of carbon or less, the tendency being to use mild steel rather than a medium carbon steel with, say, 0·4 or 0·5 per cent. of carbon. The furnaces most commonly used for making steel for castings are small open hearth furnaces, usually acid lined, or small converters, usually of the “surface-blown” type. In the open hearth furnace better control over composition and temperature is possible than in a converter, although surface-blown steel is frequently used on account of its greater fluidity.

Open Hearth Furnaces.—These are nearly always of small size for the sake of convenience and because it is difficult to keep a large quantity of steel hot while a number of castings are poured. The furnaces are usually acid lined, but basic open hearth steel is also now used with satisfactory results. The working of the furnace is practically the same for castings as for ingots, although more care is necessary in order to get the steel thoroughly dead melted and free from any over-oxidation or tendency to wildness. In most circumstances open hearth steel is the best for castings, as the temperature

composition, and general character of the steel are better under control in a Siemens furnace than in a converter. For small foundries and for intermittent work, however, small converters are usually found more convenient and economical.

Small Converters.—The use of small converters is confined almost exclusively to the production of steel for castings, and those used for this purpose are small tipping converters of a capacity of 1 or 2 tons or less, mostly side blown, such as the Robert or Tropenas converters. In side-blown converters the twyers are placed in one side of the converter in such a way that the blast either enters the metal through the surface layers or else is made to impinge on the surface. In the Robert converter the twyers are placed in the flattened side at such a height that they are just below the surface of the normal charge when the converter is vertical. The twyers are all horizontal, but are arranged at different angles in order to give a rotary motion to the bath. By tilting the converter the blast may be made to enter the surface of the metal or strike it at any desired angle. The use of the surface blast leads to complete combustion of the carbon monoxide to carbon dioxide inside the converter, instead of at the mouth, and the heat of combustion is thus made available for giving hot steel. The object of the rotary motion given to the bath is to promote uniform and rapid decarburisation and elimination of impurities. The Tropenas converter, another well-known form of side-blown tipping converter, is of the usual shape and has two rows of twyers at the side arranged so that the lower set are just above the surface of the molten metal. The twyers are placed horizontally and are designed to prevent as far as possible any rotary motion or other disturbance of the bath. The conical-shaped bottom of the converter serves the same purpose on account of the great depth of metal below the twyers. When the "blow" is started only the lower row of twyers is used until the flame appears, due to the oxidation of the carbon. At this point air is also admitted through the upper row of twyers and the carbon monoxide burnt to carbon dioxide just above the surface of the bath. The use of the upper row of twyers ensures a more effective

combustion of carbon monoxide than in the Robert converter, while the avoidance of any violent agitation of the bath gives steel with less occluded gas. The steel is said to equal open hearth steel in quality, and, in fact, the purification takes place largely by the agency of the oxidising slag maintained.

The small converters whether of the above or other patterns are usually acid lined, although the basic process may be worked in them. The metal is completely decarburised in them,* and then additions are made of ferromanganese or spiegeleisen together generally with ferrosilicon to give steel of the required grade.

A recent development of the Bessemer converter is the Stock furnace, in which oil fuel is used to melt the pig iron in the converter itself. Cold pig iron is charged into the furnace while it is tilted over, and oil is blown through pipes which are inserted through the twyers. The oil burns in the converter and melts the pig iron, the products of combustion being used to heat up a regenerator. When the metal is molten the furnace is tilted back and air heated by the regenerator is blown in in the usual fashion.

By whatsoever process the steel for castings is produced—whether crucible, open hearth, or small converter—it must be hot and very fluid in order that it may run well in the moulds. The steel must also be as free as possible from dissolved oxide and gases, which would give rise to unsoundness. It is the usual practice, therefore, to use ferrosilicon as an addition as well as ferromanganese or spiegeleisen, and the finished steel commonly contains 0·15 to 0·5 per cent. of silicon. Aluminium is frequently added for the same purpose and, weight for weight is much more effective as a deoxidiser. Too much aluminium must not, however, be used, as it leads to excessive piping.

Steel castings are made in greensand or drysand moulds. Greensand moulds are only used for light steel castings, and a good greensand of the iron foundry may be used. Drysand moulds are used for the majority of steel castings. The facing

* Frequently molten ferrosilicon is added after decarburisation and a short “after blow” given in order to increase the heat by the oxidation of the extra silicon.

sand must be more refractory than for iron castings, and a specially prepared mixture or "compo" is generally used. "Compo" is made by grinding together in various proportions some or all of the following materials: old graphite crucibles, old firebrick or silica brick, ganister, fireclay, and coke. The allowance for shrinkage in steel castings is about $\frac{3}{16}$ inch per foot, and large feeding heads must be used to ensure soundness and freedom from "draw." Owing to the relatively large amount of shrinkage in steel castings, large internal stresses are produced, and in many cases the castings are liable to crack unless relieved by the removal as soon as possible of the sand from some parts or by the removal of cores.

In order to remove internal stresses and to replace the original crystalline structure by a finer and more uniform one, steel castings are generally annealed by heating gradually and as uniformly as possible to a temperature of about 800° to 900° C., depending on the composition of the steel.

CHAPTER XVII

CASE HARDENING—WELDING

Case Hardening.—The surface of hardened tool steel is one of the best for resisting wear, but it is not possible to use high carbon steel in many parts of machinery subjected to excessive grinding or wearing action on account of the low ductility of such steel, particularly when hardened. The object, therefore, of case hardening is to obtain a tough, ductile material with a hard steel surface. The operation of case hardening consists in altering the surface layers of good mild steel, wrought iron, or alloy steel by increasing the percentage of carbon. On subsequent hardening by quenching from 800° to 900° C. the mild steel core remains practically unchanged and suffers little loss of ductility, whereas the “case,” which is practically tool steel, is hardened and provides a surface highly resistant to wear.

The importance of case hardening has increased very much within recent years, particularly in connection with cycle and motor car construction, for gear wheels, pins, bearings, chains, etc. The articles case hardened are usually forgings, castings being rarely so treated. The forgings are machined and finished to size before treatment, as little or no work can be done on them afterwards. They are then packed in cast iron boxes with the case hardening mixture—some carbonaceous material such as burnt leather—care being taken that each article is uniformly surrounded by the mixture. The boxes must be made airtight to prevent oxidation, except for a small hole through which the gases generated can escape. In cases where it is not required to case harden the whole surface, those parts which do not need treatment are covered with clay, loam, or other neutral material. When the boxes have been charged and prepared they are heated in furnaces of the muffle type for several hours, the time depending on the depth of case

required. The temperature used is between 800° and 1000° C., usually about 900° C. or a little less. The boxes are then removed from the furnace and allowed to cool. When cold the carbonised articles are taken out of the boxes, reheated to about 850° C., and quenched in water or oil. In some cases the carbonised articles are quenched from the boxes without a separate reheating, but it is preferable to allow them to cool slowly

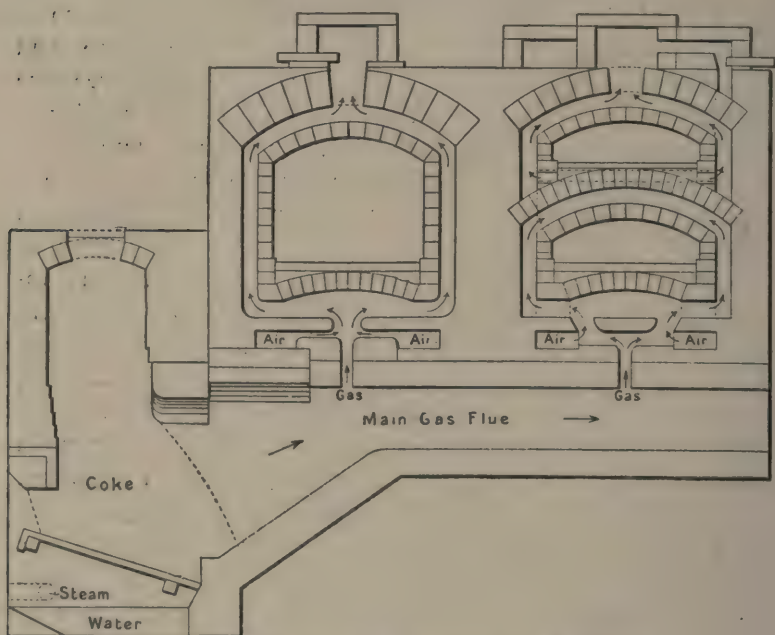


FIG. 46.—Gas-fired Muffle Furnace for Carbonising
(Case Hardening Process).

reheat, and quench, as better and more uniform results are then obtained.

The steel used for case hardening is, as has already been stated, mild steel or alloy steel low in carbon, and the analyses, on page 148, are of some suitable steels.

Among the carbonising materials used in case hardening, are : Bone-black, burnt leather, barium carbonate and charcoal, potassium ferrocyanide, acetylene gas, oil or coal gas, and

carbon monoxide. In addition there are a number of compositions sold under trade names.

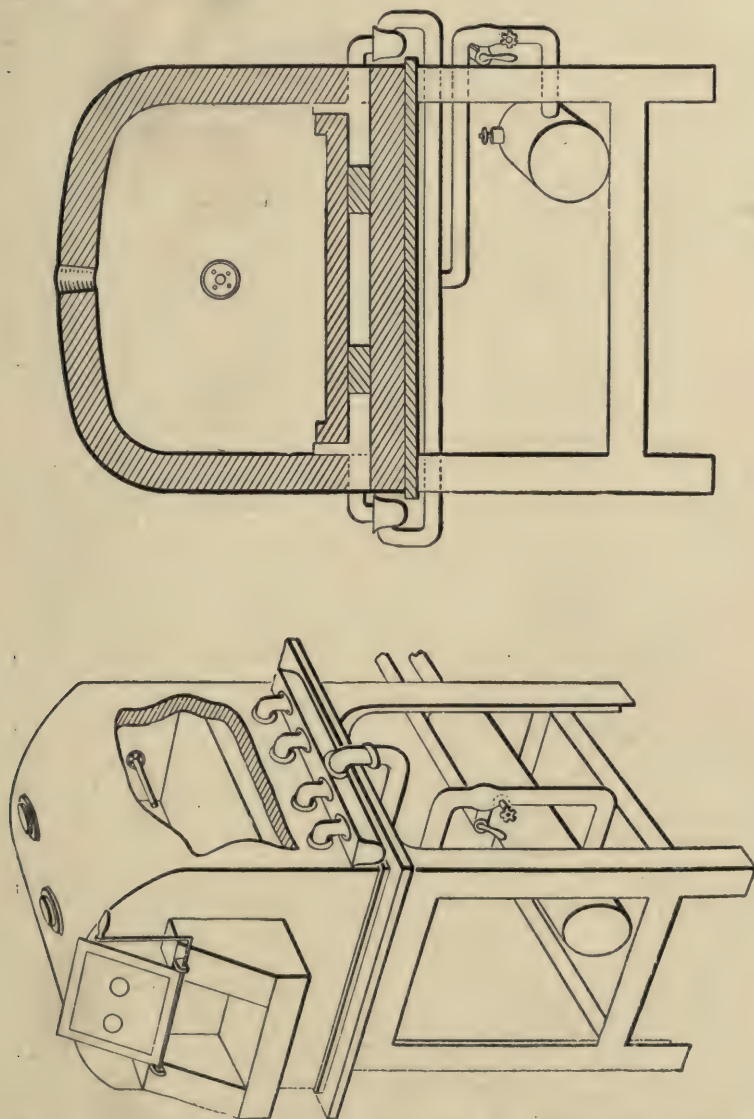


FIG. 47.—American Gas Muffle for re-heating the carbonised work for quenching (Case Hardening Process).

From the results of much recent work on the subject it appears to be conclusively proved that the direct penetration of pure carbon into iron is exceedingly slow (if it occurs at all), and that carburisation takes place through the agency of carbon monoxide or gaseous hydrocarbons. The presence of nitrogenous compounds, particularly cyanogen derivatives, adds greatly to the carburising power of carbonaceous materials, and most of the mixtures used consist wholly or in part of carbonaceous material of animal origin. In using gaseous carburising agents the depth and character of carbon penetration may be controlled by suitable variations of pressure, and

EXAMPLES OF STEELS USED FOR CASE HARDENING.

—	Mild Steel.		Nickel Chrome Steel.
Carbon	0·12	0·14	0·33
Silicon	0·06	0·01	0·06
Sulphur	0·02	0·08	0·02
Phosphorus	0·03	0·03	0·02
Manganese	0·47	0·58	1·15
Nickel	—	—	1·17
Chromium	—	—	3·50

the work of Giollitti and others, an account of which has been published in the *Journal of the Iron and Steel Institute* for 1911 (Vol. II.), has shown that exceptionally good experimental results are obtained in the carburisation of mild steels and alloy steels by means of carbon monoxide under properly controlled pressure.

Welding.—The operation of welding iron or steel consists in uniting two clean surfaces by hammering them together when at a high temperature. A special form of welding known as autogenous welding consists in uniting two pieces of metal by melting new metal into the joint and thus actually fusing them together. The property of welding is characteristic of wrought iron. Mild steel also is readily welded, but as the amount of carbon increases, and the steel is more easily burnt, welding becomes more and more difficult. The presence of impurities decreases the welding power of steel. Small

quantities improve the welding quality of steel, but steel with larger quantities and alloy steels generally are very difficult to weld.

The operation of welding involves the heating of the two ends to be joined to a very high temperature, usually approaching the melting point, and consequently leads to local overheating. The effect of this overheating may be more or less completely removed by hammering during welding and while the metal is cooling, but, even if the actual weld is perfect, the metal in its neighbourhood nearly always suffers deterioration. Most hand welds show a reduction, frequently to the extent of 40 or 50 per cent. of the tensile strength or ductility, or of both.

In addition to the ordinary method of welding by heating in a smith's fire, other methods are used which may be referred to briefly.

Electric Welding.—This is of two kinds—resistance welding and arc welding. Resistance welding, which is a true welding operation, consists in placing the two ends which are to be joined in contact, heating them to a welding heat by electrical resistance, and then pressing the two ends together. The weld is finally hammered during cooling to reduce the effect of local overheating. Arc welding, which is an example of autogenous welding, involves the actual melting of the two ends and the filling of the space with metal melted from a rod.

Thermit Welding.—By this process molten iron at a high temperature is produced by the reduction of oxide of iron with powdered aluminium and then allowed to run into the space between the two ends to be welded. This method requires the preparation of a suitable mould surrounding the weld.

Welding with Gases.—The high temperature of the flame produced by the combustion of acetylene, or by the combustion of hydrogen, coal gas, or water gas in oxygen, is used to heat the two ends to be welded. In welding with gases an intense local heat is produced, and the usual overheating effect may be confined to a very short distance on either side of the weld. With acetylene a strongly reducing flame may be obtained with the production of a clean weld, and no local decarburisation is produced, such as is the case where an oxidising flame is used.

SECTION II

THE CORROSION OF STEEL AND IRON

By GUY D. BENGOUGH, M.A., D.Sc.

THE general nature of the action which takes place when iron or steel rusts and corrodes is now fairly well understood, although several points of great academic interest still remain to be cleared up. The problem of chief interest to engineers is the elucidation of the factors that determine the rate and character of the corrosion in any particular case. It has gradually become evident that these are of the most diverse and complicated kind. At least a dozen influences have been shown experimentally to exert important effects, and for a complete understanding of the whole problem it is necessary that all these should be studied, not only separately, but two, three, and four at a time. By far the greater part of this work remains to be done, and it will only be possible here to deal in outline with the problems involved.

In the early days of chemistry it was thought that the rusting of iron and steel was the result of a direct attack by the oxygen of the air. Later it was discovered that dry air had no action at the ordinary temperature; and Friend has shown that even at 100°C . the action is quite slow. At higher temperatures the well-known "temper colours" are formed in dry air, and appear to be due to the direct formation of FeO , which is gradually oxidised to Fe_2O_3 in layers the thickness and colour of which vary with the temperature. The composition of ordinary rust, however, does not correspond with either of the formulæ given.

In 1845 Adie showed that iron might be kept in water quite free from air for six months without showing oxidation, and concluded that no iron passed into solution. In 1903 Whitney confirmed this observation and found that iron could be kept

indefinitely in water free from air without showing any trace of oxidation.

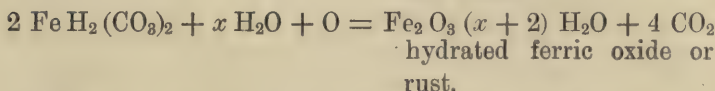
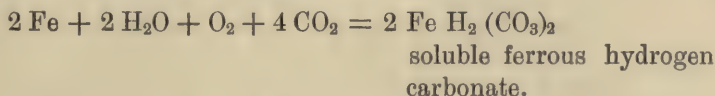
In 1910 Lambert and Thomson* showed conclusively that *pure* iron will not rust in contact with *pure* oxygen and *pure* water. Yet it is a fact familiar to all, that rust will form on iron or steel in the presence of *ordinary* air and moisture. What, then, are the conditions under which rusting will take place?

For a long time it was thought that atmospheric rusting was due to the presence of carbon dioxide in the air, since this gas would pass into solution in all ordinary samples of water, giving rise to carbonic acid which would attack the metal.

The facts mentioned would seem at first sight to support strongly an acid theory of corrosion, which would postulate that, in addition to oxygen and water, the presence of an acid should be essential to corrosion.

Such an acid theory of corrosion was originally put into coherent form by Crace-Calvert, and in recent years has been ably defended by J. Newton Friend.

This theory may be expressed approximately in the form of chemical equations as follows:—



It will be seen that four molecules of acid only are necessary to start corrosion, and that after once being started the process may become continuous, since the acid is regenerated.

Herein lies the difficulty of either proving or disproving this theory, for chemical tests are not delicate enough to detect such minute quantities of acid as are sufficient to start corrosion according to this theory. It is, however, certain that corrosion will go on at fairly rapid rates even when the most delicate tests now known to science fail to detect the presence of an

* For references, see list of papers at the end of the Chapter.

acid. A further difficulty in the way of this theory has been recorded by Lambert, who finds that pure iron will not rust in contact with pure water, oxygen, and carbon dioxide.

On the whole, therefore, it would appear to be best to regard an acid as an accelerator of corrosion, rather than its initiator and essential cause, and it becomes necessary to look elsewhere for a satisfactory explanation of the whole problem.

It will be convenient now to sum up the results already recorded as to the chemistry of corrosion.

Dry air, and presumably dry oxygen, have no action on iron at the ordinary temperature.

Air-free water has no action under similar conditions.

Pure water and pure oxygen have no action on pure iron.

Ordinary samples of iron and steel rust in the air in the presence of moisture.

The presence of an acid is not essential to corrosion.

The conclusion to be drawn from these statements appears to be that in addition to water and oxygen the impurity of the substances concerned must be closely connected with the initiation of corrosion. Davy appears to have been the first to base a theory of corrosion on this principle, and in recent years Tilden has ably advocated it. This theory is known as the electrolytic theory of corrosion. On this theory rusting can only take place when the iron is not uniformly pure; one part at least must be capable of becoming electro-negative to another. In addition to this the water must be sufficiently impure to be a conductor.

Under these circumstances the following action can take place. Ferrous iron will pass into solution at some part of the metal which happens to be electro-positive to the neighbouring portions; hydrogen or some more electro-positive metal will pass out of solution at a corresponding electro-negative area, since iron can turn out of solution hydrogen and all metals lower down than itself in the electro-potential series. The action is similar to that of a Daniell cell, the iron corresponding to the zinc, the hydrogen to the copper that plates out of the copper sulphate solution, and the electro-negative area to the copper cylinder of the cell. The external circuit that must be

made before the Daniell cell will pass any current is formed in the case of a corroding metal by the mass of the metal itself, and is of course permanently closed.

The electrolyte of the Daniell cell consists of a solution of copper sulphate, and this corresponds to the water or moisture in ordinary cases of corrosion. This water must be sufficiently impure to possess a fair amount of conductivity, or its resistance will be too high to allow the little current generated by the cell to pass, in which case the whole action will stop. It will now be obvious why certain acids and salts which increase the conductivity of water also increase the speed of corrosion.

Thus the essential conditions for rusting to take place are seen to be :

The iron must not be uniformly pure.

The impure portion must be capable of conducting electricity.

The water or moisture must be sufficiently impure to be a conductor.

It should be noticed that on this theory pure iron placed in water containing carbon dioxide would not rust ; neither would impure iron in ideally pure water ; the reason in both cases being that no electric current could be started.

The function of the oxygen in corrosion has still to be dealt with. This substance has at least two important actions, which will now be explained in detail. Corrosion may be defined as the passage of the metal into solution, while rusting is its subsequent precipitation as a hydrated ferric oxide. One function of the oxygen is evidently to oxidise the soluble ferrous iron to the insoluble ferric oxide. The removal of the iron from solution in this way prepares the way for the entrance of a further amount of iron into solution and so helps the process of corrosion.

It is a well-known fact that corrosion goes on at an increased rate when rust has once been formed on the surface of a metal. This has been explained as being due to the fact that rust is electro-negative to metallic iron, and so helps to form the electro-negative area of the little electric circuits which set up corrosion.

Many chemists believe that oxygen also assists corrosion in quite a different way. It has already been pointed out that when iron passes into solution in an ordinary sample of water hydrogen is displaced from solution. This hydrogen will appear in the gaseous form at the electro-negative areas which form the cathodes of the little cells. Now the presence of a film of hydrogen gas in the circuits will introduce into them a resistance of great magnitude, and this may be so large as to prevent any current from flowing at all. But if oxygen can obtain free access to the hydrogen at the moment when it is passing out of solution it may oxidise it to water and so prevent the formation of a resisting film. Corrosion can then proceed actively.

When the action of a little cell has been stopped by the formation of a film of hydrogen in the way described, the cell is said to be polarised. Any substance which can remove the film and restart the action is said to be a depolariser. Thus oxygen must be considered to be a depolariser.

The subject up to this point may be summarised as follows :—

Ordinary metals dissolve or corrode owing to the fact that they are not chemically homogeneous.

Any impurity present in the metal may set up corrosion, provided that it can conduct electricity.

In general a metal will be corroded by a liquid which contains hydrogen ions or ions of a metal less electro-positive than itself.

When the corroding iron is displacing hydrogen from the solution the action will be accelerated by the presence of a depolariser, *i.e.*, some substance which will rapidly remove by oxidation or other means the displaced hydrogen. Such a depolariser may be present in the corroding liquid or in the corroded metal.

The nature of the surface of the metal may influence the speed of corrosion. If the surface be of such a nature as to facilitate the formation and removal of hydrogen gas, it will also facilitate corrosion.

It has long been known that under certain conditions iron is capable of assuming a state in which it is much less chemically

active than is normally the case. To this condition of comparative chemical inertness the name "passive state" has been given. A large number of reagents are able to induce this state in iron, but perhaps the best known are chromic acid, potassium bichromate, potassium hydroxide, and potassium chromate.

No very obvious change on the surface of the metal accompanies the change from the active to the passive state, and chemical reactions must be employed to detect it. In a recent and detailed paper on the subject Dunstan and Hill have found the following reagents most useful for detecting passivity :—

A solution of nitric acid ; specific gravity 1·2.

A solution of copper sulphate ; strength 0·5 per cent.

Immersion of the iron in distilled water and observation of the time elapsing before rusting begins.

Nitric acid readily attacks ordinary, *i.e.* active, iron with effervescence. Passive iron is not so attacked, and remains perfectly bright and immune for times varying from a few seconds to several hours. Copper sulphate at once deposits a film of copper on active iron ; passive iron will remain perfectly bright in the solution for considerable periods of time. Active iron rusts visibly in distilled water exposed to the atmosphere in about eight or ten minutes ; passive iron will remain for one or two hours before rusting begins.

If passive iron be scratched with a glass rod or touched with a piece of active iron it immediately becomes active at the point of contact, and the action spreads visibly over the whole surface. Shaking or any other rough mechanical treatment also destroys the passive state.

It is evident that there is an intimate connection between the phenomena of corrosion and rusting and of the passive state. For instance, those reagents which induce the passive state inhibit, that is temporarily prevent, the process of rusting. Consequently a knowledge of the nature and causes of the passive state becomes of great importance in the study of corrosion.

Many theories have been put forward to account for the phenomena of passivity. Most of them are based on the supposition that a protecting film is formed on the surface of

the metal. Some consider that the protecting layer consists of metal that has been changed in some way, as, for instance, from the bivalent to the trivalent state. The general consensus of opinion appears to be that a layer of magnetic oxide is formed all over the surface of the metal. This layer is very thin and easily broken mechanically, and, compared to iron itself, would be chemically inert.

In support of this view may be mentioned the fact that many of the reagents which produce the passive state are powerful oxidising agents.

A large number of chemical reagents rapidly destroy the passive state, and so increase the rapidity of rust formation. Among the more important of these may be mentioned dilute acids—even such weak ones as acetic, formic, citric, and carbonic acids. Many salt solutions act in the same way, particularly sodium chloride and other haloid salts, and certain nitrates and sulphates.

These acids and salts not only destroy the passive state when once formed, but also prevent its formation when they are present together with passivifying agents. It seems probable that Dunstan and Hill's discovery that those reagents which prevent rusting also produce the passive state, and that many of the reagents which accelerate rusting prevent the assumption of the passive state, may form a useful starting point for investigations designed to improve the protective qualities of paints.

One of the most interesting questions in connection with the study of passivity is the cause of the inhibiting action of alkalis. If impure iron be placed in a decinormal solution of sodium hydroxide it will remain unrusted for an indefinite time. Yet all the conditions are present, apparently, for rapid rusting to take place. The oxide film theory of passivity does not seem to cover this case, since a dilute solution of sodium hydroxide is not known to oxidise the surface of the iron to magnetic oxide, as required by the theory.

Baker suggests the following explanation, based on the electrolytic theory of corrosion:—A surface of commercial iron contains impurities such as carbide of iron, phosphide,

etc. These are electro-negative to pure iron, and would form cathodes if the metal were placed in an alkaline solution. A transient electrolysis would take place, and either or both of two things might happen. The impurities might be coated with hydrogen or the pure metal might receive a superficial coating of oxide. In any case electrolysis would cease and the metal would become passive. It would thus appear that the passive state may result from widely different causes, and that, consequently, no one general explanation can be put forward that will cover all the possible cases. To show the complexity of the whole problem the following experiment of Dunstan and Hill may be quoted :—A piece of iron was placed in a dilute solution of sodium chloride containing a few drops of the indicator phenolphthalein. In the absence of air nothing happened, although sodium chloride is one of those substances that have been shown to destroy passivity. Air was then admitted, but did not form a protecting layer of magnetic oxide. On the contrary, rusting immediately began. Baker explains this by assuming that before the entrance of air the circuits were polarised as in the case considered above ; on the admission of air the polarisation of the cathode is destroyed by oxidation, and corrosion and rusting can proceed.

For the further discussion of the subject the electrolytic theory will be used as a basis, and the factors which tend to affect the rate of corrosion will be dealt with in detail.

The following factors have been shown by Friend and others to influence the rate at which corrosion takes place. In all cases moisture or water is assumed to be present.

1. The chemical composition of the sample of iron or steel considered.
2. Contact with other more or less electro-negative substances which are metallic conductors.
3. The presence of stray electric currents passing to or from the sample of iron or steel.
4. The quantity of dissolved oxygen present in the water or moisture in contact with the sample.
5. The rate of motion of the water.
6. The presence in the water of acids, salts, or alkalis.

7. The presence of previous rust.
8. The temperature.
9. The physical condition of the metal.
10. The quantity of light falling on the metal.

In addition to these factors, all of which have been proved by experiment to affect the rate of corrosion, there are possibly a number of others which have not yet been established by satisfactory experiments. It will be shown later that several of the factors in the above list depend in turn on a number of subsidiary factors. It will now be understood that the phenomenon of corrosion is most complicated and by no means a matter that can be remedied by any general process of prevention. The circumstances accompanying any given case must be considered in detail and the remedy appropriate to those particular circumstances applied, if possible. As a matter of fact, cases of corrosion occur not unfrequently which, with the knowledge at present available, cannot be remedied at any reasonable cost. Replacement of the damaged part is then the only course open to the engineer.

With these preliminary remarks a more detailed consideration of the factors given in the list may now be taken up.

1. *The influence of chemical composition.*—From what has been said in the earlier chapters of this book it will be readily understood that commercial iron and steel are by no means chemically pure. A study of the micro-photos of steel and iron will serve to remind the reader of the impurities which occur most commonly. One of the most convenient ways of studying the influence of these substances on corrodibility is by means of the “ferroxyl” indicator, the use of which was first suggested by Walker and Cushman.

This indicator is made by neutralising an aqueous solution of gelatine, which would just set on cooling, with caustic soda, and adding a little potassium ferricyanide and phenolphthalein. It is used in the following way: The sample of iron or steel is carefully cleaned and roughly polished, and then placed in a porcelain dish. The hot solution (prepared as directed above) is then poured over the sample in sufficient quantity to com-

pletely cover it. The whole is then set aside to cool and solidify.

The action of the indicator is as follows : If corrosion take place at all, iron will pass into solution at electro-positive areas of the iron and will react with the potassium ferricyanide, forming iron ferricyanide, which is of a deep blue colour. This reaction causes potassium to be set free. The potassium will immediately react with water, forming hydrogen and potassium hydroxide. The potassium hydroxide will be detected by the formation of a pink colour with the phenolphthalein. Consequently, electro-positive or anodic areas, at which iron is passing into solution, will be indicated by the appearance of a blue colour. Electro-negative or cathodic areas will be denoted by a pink colour.

It will be obvious that this test can be used in a great variety of ways for the study of corrosion. The following are some of the more important results obtained with it by Cobb and others :—

Pure iron is electro-positive to most of the impurities which commonly occur in it. Among these may be mentioned graphite, ordinary free carbide, and the phosphide, sulphide, oxide, and silicate of iron. Most iron alloys, except ferromanganese, are electro-negative to pure iron.

The sulphide and silicate of manganese, both of which may occur in iron and steel, do not set up corrosion, since they are both non-conductors of electricity. Metallic manganese and 80 per cent. ferromanganese are electro-positive to iron, and, consequently, themselves pass into solution when in contact with iron, the iron being protected from corrosion.

It is to be particularly noticed that the distribution of the impurity is almost as important as its total quantity. Each small fragment constitutes a centre of corrosion. A fairly large mass is, in this respect, no more harmful than a small portion. Thus the nature and distribution of the impurity may be of more importance than its total quantity.

The supreme influence of carbon on the properties of iron and steel has been clearly shown in the earlier chapters of this book. This substance is an essential constituent in almost all varieties

of these metals. A study of the influence of carbon on the rate of corrosion is therefore of great importance, both from a scientific and a commercial point of view. A committee of the British Association have recently published the results of an investigation into the matter, and their conclusions may be summarised as follows :

In the case of rolled and annealed material, the corrosion of pure carbon steels by sea-water increases with increase of carbon up to the eutectoid proportion, 0.89 per cent. In the case of quenched and tempered steels corrodibility increases with the carbon content up to 0.96 per cent., which was the maximum proportion used in the experiments.

It is to be remembered that heat treatment may bring about great changes in the form in which the carbon exists in a sample of iron or steel, and it is therefore to be expected that heat treatment would also affect the rate of corrosion. This has been shown to be the case by Chappell, who concludes that a sample of steel shows maximum corrodibility when quenched, and minimum when annealed. The corrodibility of tempered steels varies with the tempering temperature, and is usually intermediate between those of quenched and annealed steels.

2. *The influence of contact with other more or less electro-negative substances.*—In general, contact with a more electro-positive substance will result in the protection of the iron or steel. On the other hand contact with a less electro-positive substance will intensify the attack on the iron or steel. It has been known for some time that a difference in the physical condition between two parts of the same piece of metal may result in one of them being more electro-positive than the other ; such differences may thus give rise to what may be called self-corrosion. The difference in physical condition may be due to a variety of causes. One of the most important of these is the difference in the amount of mechanical work put upon the various parts of the same piece of metal. It has been shown in the earlier chapters of this book that the greater the amount of mechanical work put upon a metal the harder it

becomes, and these differences in hardness may be sufficient to set up corrosion.

Experiments with the ferroxyl indicator have shown that almost any sample of commercial iron, when placed in contact with any other, will show that electrical differences exist between the two. This really means that when any two samples of iron are in contact with one another the rate of corrosion of one of them will be increased. If the two samples happen to be alike in character the effect will be very slight. Thus when two samples of rail-steel are in contact with one another the increase in corrodibility of the more electro-positive of them will usually be negligibly small. But wherever a steel cast-iron junction exists, in the presence of moisture, active corrosion will usually be set up. Similarly a steel-brass contact will be very liable to corrosion, the steel being actively attacked. On the other hand a steel-zinc or steel-aluminium junction will result in the preservation of the steel at the expense of the zinc or aluminium, since both these metals are more electro-positive than iron or steel. The principles here discussed are obviously capable of considerable extension, and have an important bearing on many of the problems of corrosion which occur in practice. Thus masses of zinc may be used in boilers to protect the shells from corrosion. It should be mentioned, however, that the protective action of zinc does not extend to any great distance away from itself.

3. *The influence of stray currents passing to or from a sample of iron or steel.*—Owing to the widespread use of electricity for power and lighting purposes, there is always the possibility of a leakage of electricity to or from rails, pipes, and other conductors buried in the ground. Without going into this part of the subject in any detail the general result may be stated to be that wherever a current leaves a metal to enter the ground corrosion will take place at an accelerated rate. Wherever a current leaves the ground and enters the metal the latter will be protected. These principles may be extended, with suitable modifications, to meet all kinds of cases of corrosion in which stray currents are involved, such as the corrosion of the iron

bodies of condensers. The reader should be able to work out the nature of the action occurring in any particular case.

4. *The influence of the presence of dissolved oxygen or air in the water or moisture in contact with the metal.*—The general effect is that the greater the quantity of oxygen present the more rapidly will corrosion proceed. Thus, corrosion is always more active at the surface line than below it, wherever iron pillars are immersed in water. In this connection it may be mentioned that some forms of water-cooling and condensing apparatus deliver their water highly charged with air. If this be passed straight into a boiler the latter will be rapidly corroded; consequently it is advisable in such cases that the water be passed through some form of preheater which will remove by evaporation the greater part of the air.* As regards the corrosion of iron piping, it should be noticed that at bends and similar places where air can collect, or an airlock be formed, corrosion will go on at an accelerated rate. This fact is frequently overlooked by designers, and is sometimes the cause of serious trouble, for corrosion once started goes on at an increasing rate, and will in time necessitate the redesigning of the pipe line.

It may be mentioned that an increase in temperature lowers the amount of oxygen that can be held in solution in water at the ordinary atmospheric pressure. On the other hand chemical activity increases with rise of temperature. Consequently the rapidity of corrosion will reach a maximum at some temperature which is not very high. Heyn and Bauer have shown it to be 80° C. for distilled water.

5. *The influence of the rate of motion of the corroding water.*—In general the more rapid the motion of the water the more rapidly will corrosion proceed. This arises from the fact that the process of corrosion rapidly exhausts the supplies of oxygen in the neighbourhood of the corroded metal. But if the corroding water be in rapid motion additional supplies of oxygen will be quickly brought to the corroding areas, and the action can proceed continuously and rapidly.

* Filters of charcoal may also be used to remove air, since charcoal has the property of absorbing gases.

6. *The influence of the presence of acids, salts, and alkalis.*—This portion of the subject is far too vast to be discussed here in any detail. A large amount of work has been done on it by Friend, and reference should be made to his papers, published in the *Journal of the Iron and Steel Institute*, by all who are specially interested in the subject. All that can be done here is to record the following general statements:—

1. The general effect of dilute acids is to accelerate the speed of corrosion. Strong acids may, in certain cases, inhibit it.
2. Dilute solutions of many salts increase the speed of corrosion. Stronger solutions, by decreasing the solubility of oxygen, may reduce the rate of corrosion. Consequently there is usually for each salt a definite concentration which gives rise to a maximum rate of corrosion.
3. Alkalis, when present above a certain small concentration, inhibit corrosion. Very dilute solutions of alkali, however, do not seem to do so, and this fact is somewhat difficult to explain on the electrolytic theory of corrosion.

There are a number of exceptions to these general statements. For instance, dilute solutions of the salts which produce the passive state will obviously retard corrosion. Taking advantage of this fact, Friend has proposed to add from 10 to 100 lbs of potassium chromate to every 1,000 gallons of water introduced into boilers, the exact amount being adjusted to the corrosive properties of the particular sample of water.

7. *The influence of the presence of previously formed rust.*—Rust once formed increases the speed at which corrosion proceeds. The rusted areas probably constitute electro-negative poles, and so enhance the speed of corrosion of the surrounding electro-positive iron.

8. *The influence of temperature.*—The effect of an increase in temperature is, in general, to accelerate the speed of chemical change, and for this reason might be expected to increase the

speed of corrosion. On the other hand, an increase of temperature causes a decrease in the solubility of oxygen in water and most salt solutions, and this will result in a decreased rate of corrosion. The total effect of these two opposing factors will usually be that speed of corrosion will reach a maximum at a particular temperature which will depend on the exact nature of the corroding liquid.

9. *The influence of the physical condition of the metal.*—It seems probable that highly worked or strained metal is more liable to corrosion than softer material. This probably results from the facts that the work-hardness of the metal varies from point to point, and that the harder or more highly strained portions become electro-positive to the neighbouring parts. The more highly strained parts will thus be more liable to corrosion. It is, however, necessary to mention that the experimental evidence in this connection is not quite as clear as could be wished.

10. *The influence of the quantity of light falling on the metal.*—Friend has published a number of experiments which tend to show that the greater the quantity of light falling on a sample of iron or steel the more rapid will be the corrosion. It does not seem probable that the effect of this factor is very great from a practical point of view.

The Protection of Iron and Steel from Corrosion.

The enormous complexity of the subject of corrosion will now be abundantly evident to any reader who has followed the subject up to this point. It is largely owing to the great number and varying nature of the factors that influence corrosion that so many difficulties are met with in any endeavour to prevent it. The exact circumstances which surround any particular case of corrosion must be carefully studied before any protective measures can be devised, and it will only be possible here to deal in a very general way with the question of the protection of iron and steel against corrosion.

The condition essential before corrosion can take place requires actual contact between the metal and a corroding

liquid. The possible means of preventing corrosion may therefore be conveniently considered under three heads :

1. An alteration in the composition of the metal so as to render it less corrodible.
2. The prevention of contact between the metal and the liquid.
3. An alteration in the composition of the liquid so as to render it less corrosive.

With regard to the first of these preventatives not very much information has been accumulated at present. It may be said generally that the purer and more homogeneous the iron the less will be its liability to corrosion. Exceptions to this statement must be made in the case of certain of the alloy steels, such as nickel and chromium steels. Nickel steel, in particular, seems to resist corrosion both by acid and neutral corroding liquids. Its power of resistance appears to increase with the amount of nickel present, at any rate up to 26 per cent. of nickel. Chromium, in amounts up to 4 or 5 per cent., appears to be particularly useful in enabling steel to resist the attack of a neutral medium, such as sea-water. On this account Friend and his co-workers have suggested its extended use in the construction of ships.

Many other kinds of special steel will probably be discovered to be resistant to corrosion either by sea-water or ordinary moisture. The drawback to the employment of such materials at present is that of expense. It is probable, however, that a greatly increased demand would enable them to be produced much more cheaply by stimulating the search for new ore deposits, and by causing further search for improvement in methods of manufacture. The writer looks forward to the time when practically all steel will be incorrodible.*

Until the dawn of this era, the second and third methods of prevention above mentioned must be relied upon, except in special cases where expense is of secondary importance.

Contact between the metal and the corroding medium may

* What is really required is a steel that shall be resistant to corrosion and yet at the same time be cheap to machine, and not easily spoilt in the reheating and rolling processes.

be prevented by coating the metal with some material which is impervious to moisture and liquids. Such a coating may consist of a metallic substance, a paint, or an oxide.

Of metallic coatings the most generally used is zinc. This may be deposited on the iron either by dipping sheets into a bath of molten zinc, or by an electrolytic process. A third method is sometimes used, especially for small articles. It consists in placing the articles together with zinc dust in an airtight iron drum, which is then heated to a low temperature and rotated slowly. Zinc vapour is formed under pressure in the interior of the drum and deposits a very coherent and uniform coating on the surface of the iron. This process is known as "sherardising," after the name of the inventor.

Zinc forms an efficient protection to the iron as long as the coating remains intact. If the coated material be bent at a sharp angle the coating is liable to be cracked and broken, and corrosion of the exposed iron may then begin. This is particularly liable to happen in the case of wire. It should be noticed, however, that zinc is electro-positive to iron; thus, when the iron has been once exposed the zinc coating will be rapidly eaten away, and the iron will still be temporarily protected; but when a considerable area of the iron has been exposed it will be no longer preserved, since the area over which the zinc can exert its protective action is a restricted one.

Tin is sometimes used as a protective coating. It is more expensive than zinc, but forms a denser and more effective coating. It is electro-negative to iron, and the result is that, if by any chance a part of the iron be exposed, active corrosion will take place at that point.

The subject of protective paints is too large to be dealt with here. It may be useful to point out, however, that they may act in two ways—first, by the mechanical prevention of contact between the metal and corroding liquid, and, second, by the presence of some substance, such as a chromate, which will induce the passive state in the metal. The chemical and physical study of protective paints is a matter that is receiving great attention in many parts of the world and is likely to produce important results in the not distant future.

Many interesting and important facts have already been brought to light. One or two only can be mentioned here.

Pigments usually consist of a binding material and a pigment incorporated in it. The ideal binding material should contain no water and should be moisture proof. It usually consists of boiled oil. The pigment consists of ground particles of some suitably coloured oxide or other body such as graphite or chromate. In practice the binding material is never quite moisture proof; hence moisture will in time penetrate to the metal. Further, coarse particles of pigment may come into contact with the metal and set up galvanic action in the presence of this moisture. Consequently, fine grinding of the pigment, and thorough incorporation with a binding material as free as possible from water, will assist in preventing corrosion. The choice of a pigment which will not have any great tendency to set up corrosion, is also important, and a pigment such as potassium chromate, which induces the passive state, will be especially useful. Where protection of the underlying metal is of first importance and decoration a secondary consideration, a mixture of rouge and lampblack, ground to impalpable powder, and well mixed with pure boiled linseed oil with very little turpentine, has been suggested as a satisfactory material. Such paint should be applied to the cleaned surface of the iron and should be renewed as soon as its surface becomes cracked.

A protective coating of oxide may be formed on the surface of the metal by oxidising the iron itself. Thus if, under certain conditions, steam be allowed to act on a bright, hot surface of steel, a uniform layer of magnetic oxide will be formed all over the surface of the metal, giving it the well-known blue tint. This is the principle of the Bower-Barff process. The oxide coating affords considerable protection to the metal as long as it can be maintained unbroken.

Methods of protection based on a lowering of the corrosive properties of the corroding medium are, of course, not available in many cases in which atmospheric corrosion, or attack by sea-water, is involved. They may, however, be employed with advantage in certain cases of boiler corrosion. The

addition of an alkali to the feed water, for instance, may be useful, quite apart from its effect in removing hardness, and reference has already been made to the inhibiting action of alkalis. Potassium hydroxide would appear to be the most suitable substance to employ for the purpose. Friend's suggestion of the use of potassium chromate may also be mentioned in this connection.

A list of a few of the most important of recent books and papers on corrosion is appended.

"The Corrosion of Iron and Steel." J. Newton Friend. Longmans, 1911.

"The Corrosion and Preservation of Iron and Steel." Cushman and Gardner. McGraw Hill Book Co., 1911.

Very complete lists of references to original papers are given in both these volumes.

Lambert and Thomson. *Trans. Chem. Soc.*, 1910, 97, 2426.

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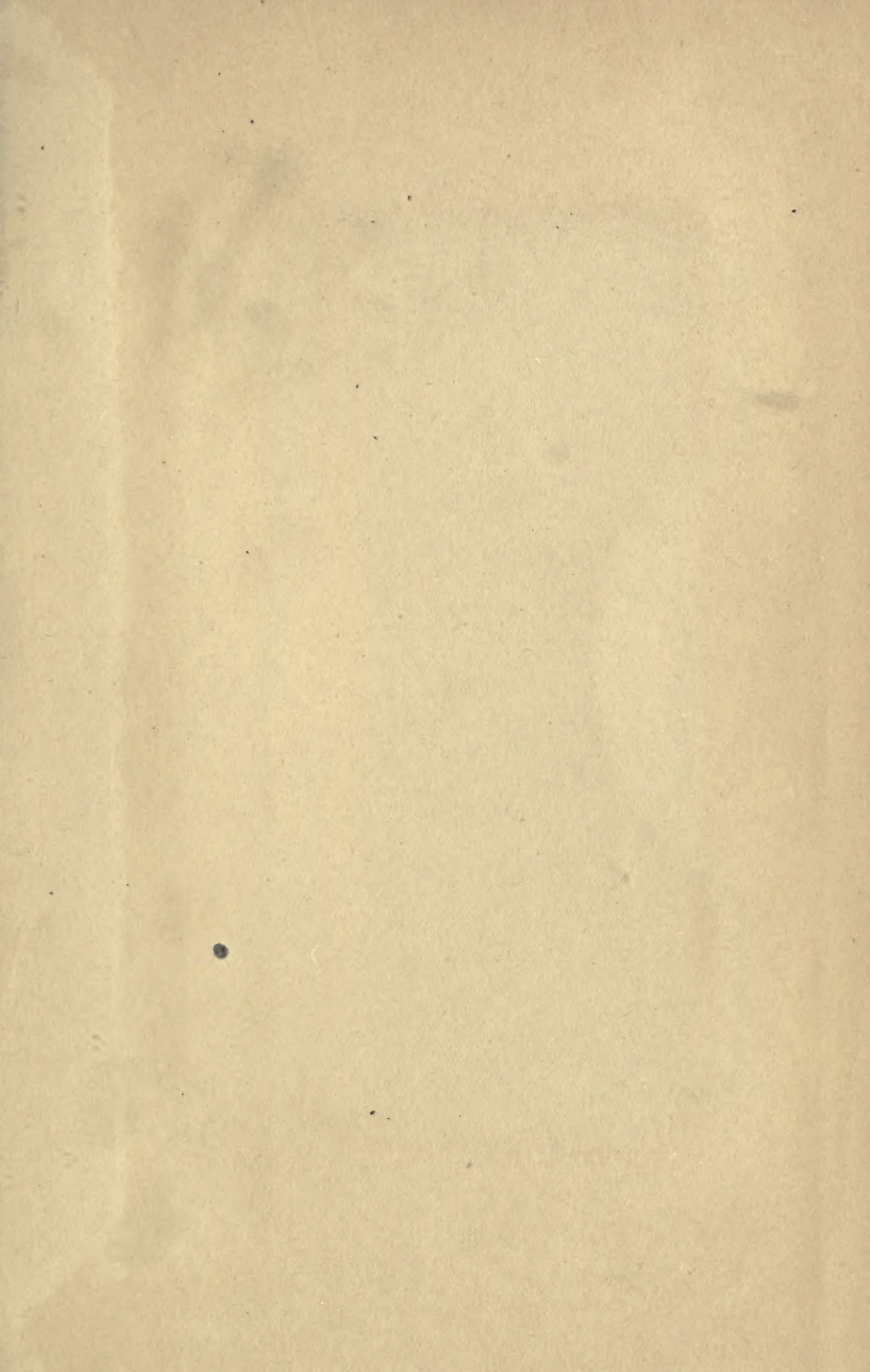
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